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**Mobility, chemical form and bioavailability of Cd, Zn, Pb and Cu in woodland soils contaminated by aerial fallout.**

# MOBILITY, CHEMICAL FORM AND BIOAVAILABILITY OF Cd, Zn, Pb AND Cu IN WOODLAND SOILS CONTAMINATED BY AERIAL FALLOUT

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A thesis submitted for the degree of Doctor of Philosophy,
University of Bristol, 1992.

## Abstract

Hallen Wood and Haw Wood are two woodlands situated about 3 km ENE and downwind of the smelting complex at Avonmouth. Contamination by heavy metals of the vegetation at both locations is principally via the processes of atmospheric deposition. The fate of the metal contaminants entering the woodland ecosystems is ultimately the soil.

The heavy metal concentrations in litter and soil profiles at both woodlands have been determined over a period of 8 years for Haw Wood and 12 years for Hallen Wood. Data for Cd, Zn, Pb and Cu at various depths in the soil profiles have been used to determine the degree to which the profiles have been contaminated and to compare the distributions of these metals down the profiles with time. The highest concentrations of metals were measured in the litter layers; however with the exception of Pb, a far greater proportion of the metal burden was located in the soil.

In Hallen Wood, Cd and Zn distributions have altered with time such that their movement has raised Cd/Zn concentrations above background soil concentrations to profile depths of about 50 cm. In comparison, Cu and Pb movement has been minimal; and no obvious signs of Cd, Zn, Pb and Cu redistribution were apparent in Haw Wood. One of the principal features of the Hallen soil profiles which would encourage the movement of Cd and Zn is the strongly acidic reaction that has been recorded in the topsoil since 1979.

Solid phase forms of heavy metals in the most recent Haw and Hallen profiles have been assessed by chemical extraction. A sequential extraction technique was employed to partition the metals into operationally defined geochemical fractions. The results from this procedure would suggest that the relative bioavailability / mobility of the metals in Haw and Hallen soils decreased in the order:

$$Cd > Zn > Cu, Pb$$

Labile, aqueous phase forms of Cd, Zn, Pb and Cu were determined by ion exchange and chromatographic techniques in conjunction with computer modelling studies. Water extracts were taken from the 1987 Haw and Hallen profiles. The results would suggest that the most mobile phase of Haw and Hallen soils was dominated by cationic species for the metals Cd and Zn, whereas for Pb and, in particular, Cu the neutral, anionic and low polar species form an important part of the solution phase.

The relative plant availability of Cd, Zn, Pb and Cu in the woodland profiles was demonstrated by growing *Holcus lanatus*

upon Haw and Hallen 1987 soils. The relative order of metal plant availability decreased in the sequence:

$$Cd > Zn \geq Cu > Pb$$

The above order is the same as the relative order of metal solubility in the woodland soils. Acidification of soil slurries demonstrated that the solubility of heavy metals increased with decreasing pH. Similarly, sunflower grown upon soils adjusted to varying pH's showed that plant uptake is influenced by changes in soil pH. These acidification studies demonstrate the role of pH in affecting the bioavailability of Cd, Cu, Pb and Zn.

In Hallen Wood, further lowering of the soil pH at depth would encourage further Cd and Zn movement down the soil profile. Considering that the Hallen soil is a heavy clay soil, the recorded extent of movement and soil contamination by Cd and Zn is a rather unusual and unexpected phenomenon.

**Acknowledgements**

Firstly, my thanks must go to the Natural Environment Research Council for financial support during this study. I would also like to thank all those in the Departments of Botany, Chemistry and Geography who have assisted me during the course of the project. In particular, I wish to thank Mike Ames for all his help in the greenhouse. I am also grateful to Dr.Smart and Dr.Whitaker for their help and advice in using Solmineq.88 . My sincere gratitude is extended to Dr. Mike Martin who has supplied me with endless support, enthusiasm, advice and often needed criticism. I am very grateful to him for his marvellous supervision.

I am also grateful to my friends and colleagues who are: Biffy, Fiona, Frank, Gill, Graham.S. and Rich.G. of Flat 51; the "biogeographers" Lynsey (and John.M.), Rebekah (and Robin), Rich.L., Sharon and Sue; the "Botanists" Ali, Debbie, Graham, Helen.R., Helen.T. , Ian (and Diane), Keith, Manjinder, Neil (Ghost), Nicky and Stuart; the "Zoologists" Andy.P., Charlie, Gareth and Anna, Jenny, Jon, Paola, Patsey, Rich.B., Roger and Avril, Steph, Tim.B., Tim.F. and Will; the "Geographers" Fiona.S., Fiona.W., Rebekah, Rich.L.; the "Mont Blanc team" Andy.S., Elsa, Ian, Jean, Jenny (H.P.), Will and Telford NSPCC; the "Shropshire lads and lasses" Andy.H. and Allison, Geoff, John.W., Mark and Sarah, and Mike and Ren; the "Pothmadoc mob" Andy.S., Diane, Ian, Jenny, John.M., John.W., Lynsey, Rebekah, Rich.L. and Robin; "Bristol Ecological Consultants" Helen, Rachel, Simon and Warren. Special thanks to Helen.T., Rich.L., Simon, Sue and Warren for all their help in the printing and typing of the thesis.

I would also like to thank Mum, Dad, Mark, "Buj" and Bryn for being so wonderfully supportive and understanding. Thanks, Joe, for all your amazing help. I am also grateful to Auntie Mercie and other friends of the family including the Field's, Hamilton's, Hyam's, Lawton's, Reece's, Thompson's, Wolskel's and Wormald's. Finally, my thanks to Geoff for all the friendship he had given throughout the years until his sad departure last year.

The research reported within this dissertation is entirely my own work except where otherwise stated,

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# CHAPTER ONE

# INTRODUCTION

## 1.1. Soils and Heavy Metals - Their Place within the Biosphere

The biosphere (ecosphere) is the term applied to that portion of the Earth that is occupied by the natural environment of living forms within the lithosphere, hydrosphere and atmosphere. The biosphere consists of ecosystems which are environmental systems containing communities of living organisms within specified areas and having balanced cycling of elements and energy flow.

Most mineral nutrients for all life in terrestrial ecosystems are supplied from the soil overlying the surficial lithosphere (Kabata-Pendias and Pendias 1984) - supply either being direct or indirect depending upon the organism. The soil is a dynamic natural body composed of mineral and organic materials and living forms in which plants grow; the soil can be further defined as a dynamic natural body having properties derived from the combined effect of climate and biotic activities, as modified by topography, acting on parent materials over periods of time (Brady 1984, Jenny 1941 - see Fig.1.1.1). In many respects the soil may be seen as the foundation of many terrestrial ecosystems and a corner-stone of human society.

Definition of a heavy metal is far from an easy task (e.g. see Hopkin 1989, Hughes *et al.* 1980, Jones and Jarvis 1981, Martin and Coughtrey 1982). Usually, heavy metals are considered as metallic elements with a specific weight higher than five (Cottenie 1980). In the context of this thesis, it is important to refine the term "heavy metal" to bear specific reference to the elements Cd, Cu, Pb and Zn. This is because the term heavy metal is not chemically revealing (Morgan 1987), and hence use of the term "heavy metal" in its most general sense could in some circumstances be misleading. Thus the term "heavy metals" can (within this thesis) be looked on as a collective term that, in particular, focuses upon the elements Cd, Cu, Pb and Zn.

Such heavy metals are widely distributed within the biosphere but usually at a low natural abundance. In the context of the ecotoxicological classification system provided by Phipps (1981) on the basis of Lewis acid concepts, such metals (Cd, Cu, Pb and Zn) would be termed "trace metals" within the soil environment (Sposito and Page 1984). Metals such as Cu and Zn are essential to biological function and are termed "essential trace elements", whereas metals

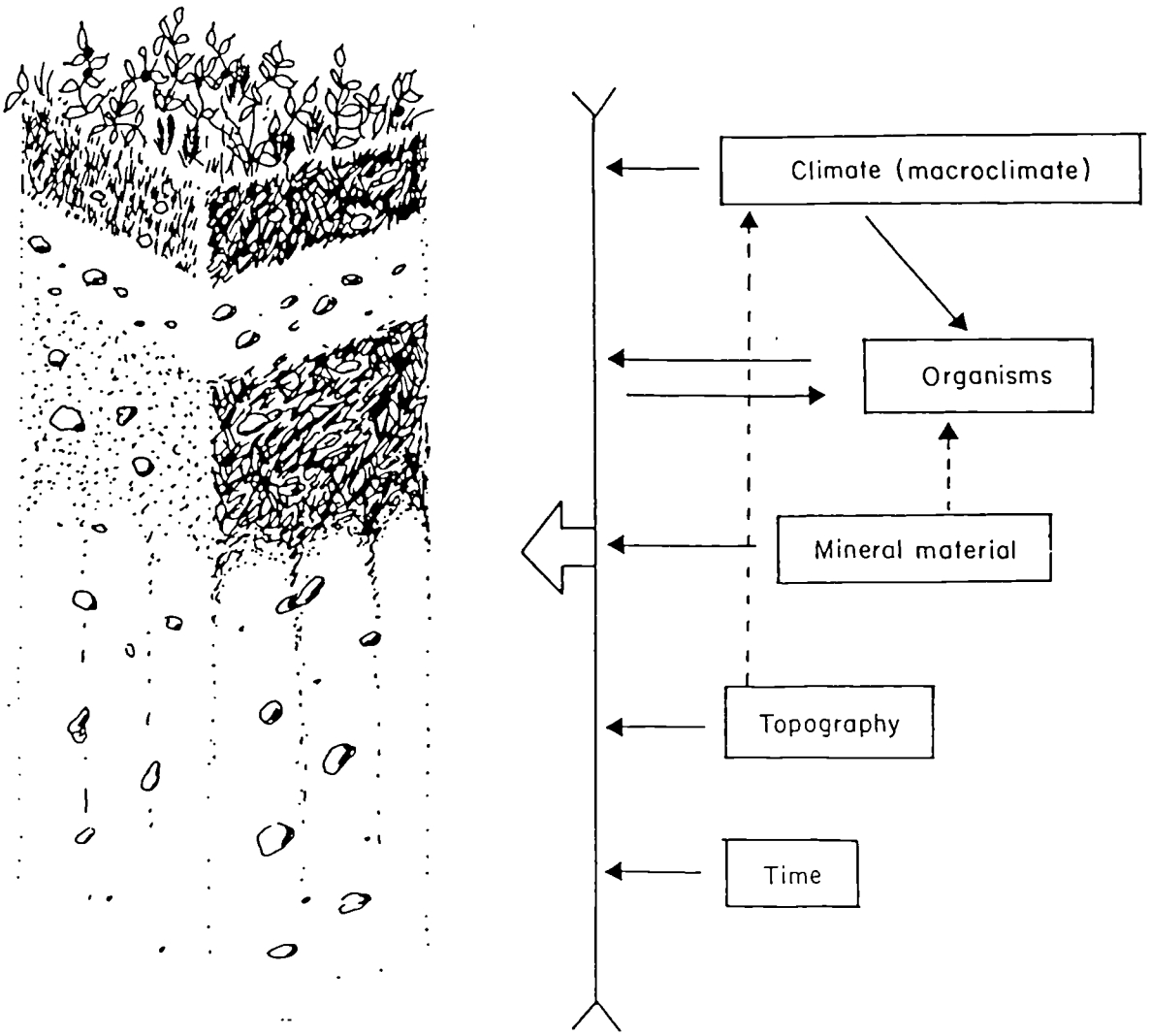


Fig.1.1.1 Schematic presentation showing the influence of soil-forming factors (after Låg 1983).

such as Cd and Pb serve no known biological function. Cd, Cu, Pb and Zn are classed as "trace elements" because they occur in concentrations of less than 1% in the rocks of the earth's crust. Usually the quantitative differences between essential/tolerable amounts and biological excesses of these heavy metals are very small. As regards Cu and Zn which are "essential" to biological function the same is true with respect to biological deficiency. In order to survive in the complex geochemical composition of their surroundings, all organisms have developed the mechanism of homeostasis by which metals may be contained at preferential levels within the organism.

Heavy metals, as environmental contaminants of terrestrial ecosystems, are not a recent phenomenon (Freedman and Hutchinson 1981) and emissions of certain heavy metals to the atmosphere as a result of human activity now rival or exceed the scale of natural emissions (Hughes 1981). Interference Factors (IF) show that anthropogenic sources exceed the flux from natural sources (IF > 1) of metal emission into the atmosphere for Zn, Cd and Pb (Nriagu 1989). In fact the ratio of the anthropogenic to natural Pb flux is so large (IF = 18) that no place on earth is now free from Pb pollution:

IF values:

| | | | |
|---|---|---|---|
| Pb = 18 | Cd = 4.8 | Zn = 2.3 | V = 1.7 |
| As = 1.6 | Hg = 1.4 | Ni = 1.4 | Sb = 1.0 |
| Cu = 0.85 | Cr = 0.71 | Mo = 0.66 | Se = 0.63 |
| Mn = 0.08 | | | |

Likewise the ratio of the annual metal mining activity to the mean metal concentration in the earth's crust (the Technophility Index or TP), suggests that the highest degree of changes of the geochemical budget by man's activities has occurred for metals such as Cd and Pb (Förstner 1987):

TP values ($5x10^7$):

| | | | |
|---|---|---|---|
| Cd = 140 | Au = 60 | Pb = 30 | Hg = 30 |
| Ag = 20 | Cu = 20 | Zn = 10 | Cr = 4 |
| Ni = 2 | Fe = 1 | Mn = 1 | |

Pollution may be defined as the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment (Holdgate 1979). Pollution of an ecosystem may be regarded as a stress imposed upon the system; the effect of which will depend on factors such as the type of pollutant, the degree of stress imposed (intensity and duration) and the resilience or response of the

most sensitive components of the system (Martin and Coughtrey 1981). Metal cycles have been profoundly modified by human activity on a regional and global basis such that certain anthropogenic trace metals and metalloids (underlined) of greater potential hazard have been identified (see Morgan 1987):

Hazardous Metals:

Cr, Cu, Zn, As, Se, Ag, Cd,
In, Sn, Sb, Hg, Tl, Pb, Bi

Many of the above metals form stable complexes with biomolecules, and their presence in even small quantities can be detrimental to plants and animals (Evans 1989). The toxicity of most heavy metals is generally associated with the inhibition of enzyme systems (Förstner 1987). The relative toxicity of metals to mammals is suggested as being (Nieboer and Richardson 1980):

Ag, Hg, Tl, Cd > Cu, Pb, Co, Sn, Be > In, Ba >
Mn, Zn, Ni, Fe, Cr > Y, La > Sr, Sc > Cs, Li, Al

The soil is a key component of terrestrial ecosystems, both natural and agricultural, being essential for plant growth, the degradation of dead biomass and the recycling of elements (Alloway 1990). The soil is a very specific component of the biosphere because it is a geochemical sink for contaminants, and in addition acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and biota (Kabata-Pendias and Pendias 1984). Asami (1984) regarded Cd as the most important metal in the soil pollution problem, because human beings consume Cd through many crops, and there is a small margin between present intake and the intake that may cause a significant effect on human health. In fact, accumulation of Cd in agricultural soils and its increased intake by plants is of world-wide concern (Förstner 1987). The toxicological importance of Cd to human health is summarised in Table 1.1.1.

The high enrichment in the natural environment of heavy metals such as Cd and Pb, their low natural abundance in the biosphere, and their high degree of "softness" as Lewis acids in aqueous reactions combine to confer unusual importance on them as toxic metals and calls for special efforts in understanding the chemistry of the speciation, fate and toxicity in natural waters and the improved chemical technology to bring about successful control of their release to the water, air and land environment (Morgan 1987).

**Table 1.1.1 The Toxicological Importance of Cadmium to Human Health**

| | |
|---|---|
| Target Organs | : Gastrointestinal tract (ingestion)<br>Lungs (inhalation). |
| Critical Organ | : Kidney (long-term exposure), 17.6 years biological half life of Cd. |
| Effect | : Interference with metalloproteins, metalloenzymes, metallothioneins and phospholipids. Stimulation of excess metallothionein production at high Cd levels and release into bloodstream. Renal tubular damage. |
| Case Example of Metal Poisoning | : Itai-itai "disease", Lower Jintsu River Basin, Japan, 1955. Derived from soil pollution. Cause due to human intake of Cd in the rice grain from Cd-polluted fields; also drinking water contamination. Source of pollution from upstream mining concern. |

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## 1.2. Anthropogenic Heavy Metal Emissions

Various natural and anthropogenic sources of metal contamination of the terrestrial environment have been outlined in several reports (eg. Alloway 1990, Freedman and Hutchinson 1981, Hutton and Symon 1987, Nriagu 1989), and some have been schematically outlined in Fig.1.2.1. Anthropogenic metal inputs due to industrial activities are a major source of metal pollution in terrestrial ecosystems and soils (Hughes *et al.*1980, Hughes 1981, Mattigod and Page 1983). The atmosphere is a key medium in the dispersal of metal contaminants and as such plays an important role in the global contamination with toxic metals (Nriagu 1989). Smelting of base metals accounts for over 50% of the Cd, Cu and Zn released from anthropogenic sources, whereas car exhaust emissions account for about 75% of the total anthropogenic Pb emissions (Nriagu and Pacyna 1988). If car exhaust Pb emissions are excluded from the synopsis of anthropogenic sources, then base metal smelting accounts for over 50% of the Pb emissions released.

The consequence of man's activity in the enrichment of his environment by heavy metals has been highlighted by certain reports (e.g. Elias *et al.*1975, Jaworowski 1968, Livett *et al.*1979, Rühling and Tyler 1968, 1969, Siccama and Smith 1978) which illustrate the increased dispersal/deposition of such metals over time and/or to remote areas distant from the source of the

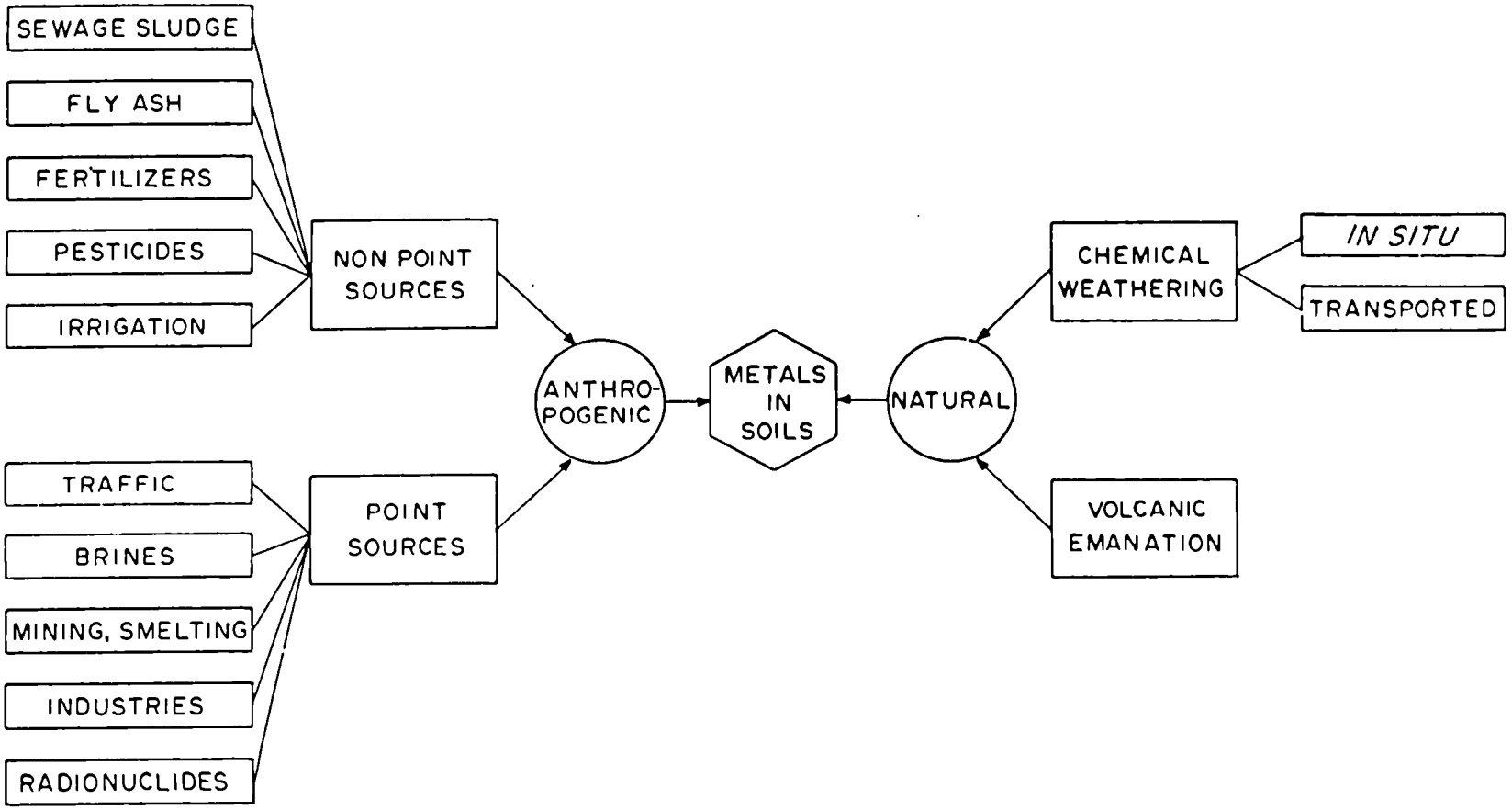



Fig.1.2.1 Diverse sources of anthropogenic and natural inputs of metals into soils (after Mattigod and Page 1983).

**Table 1.2.1 Average Annual Total Deposition of Heavy Metals at Various Sites in the UK ($mg/m^2/yr$)**

| Element | Chilton+ Oxon | Styrrup+ Notts | Wraymives+ Cumbria | Walsall‡. W. Mids | Swansea‡ S. Wales | Hallen* Wood | South Pole |
|---|---|---|---|---|---|---|---|
| Cd | <2 | <3 | <4 | <4 | <20 | 9 | <0.001 |
| Cu | 17 | 24 | 25 | 530 | 36 | 26 | 0.00 |
| Pb | 25 | 35 | 29 | 130 | 62 | 285 | 0.04 |
| Zn | 49 | 100 | 48 | 410 | 100 | 600 | 0.002 |

+ : non-urban sites (data from Cawse 1987), data collected between 1972-1981

‡ : urban/industrial sites (data from Cawse 1978, Cawse and Turner 1981)

* : woodland sites located 3-4km downwind of an industrial complex at Avonmouth, Bristol (data from Martin and Coughtrey 1981)

South pole (clean site) included from Sposito and Page (1984)

NB < values for Cd were probably limited by analytical precision.

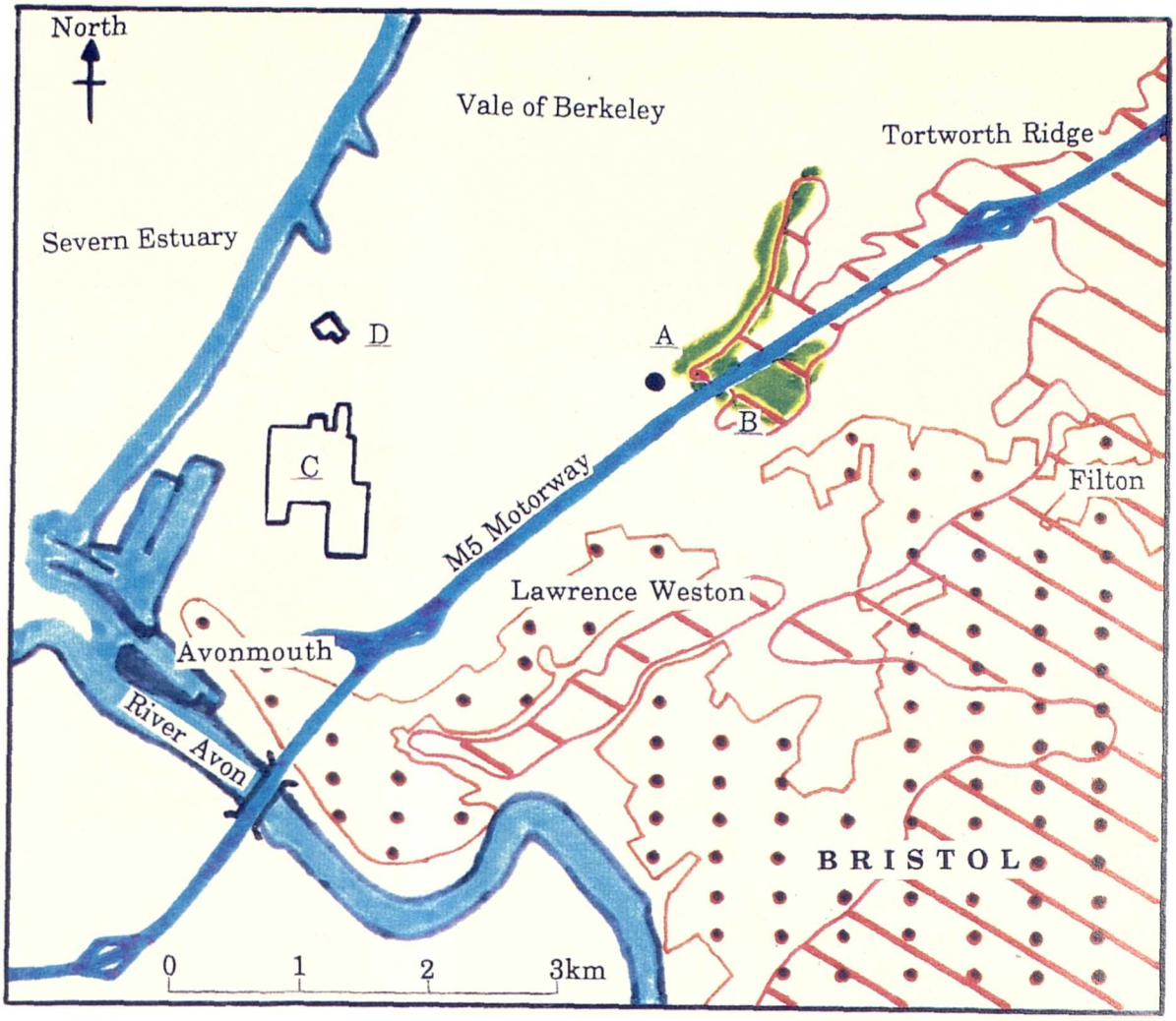
contaminant. Rates of atmospheric deposition of heavy metals, whether dry or wet, tend to be greatest near the pollution source (Hughes *et al.*1980). This is illustrated by the data presented in Table 1.2.1 which show that the non-urban locations receive lower rates of metal deposition than sites situated in or near to urban/industrial regions in the U.K. A technique frequently used as a means to evaluate natural as opposed to anthropogenic sources of deposition is to normalize air concentrations to an element with air concentrations comparable to those of the natural source providing an enrichment ratio or factor (EF) (Sposito and Page 1984). Intermediate to high enrichment factors are found for Cu and Zn, whereas the highest EF values for a wide range of metals are found for Cd and Pb (Cawse 1976, Hamilton 1974, Pierson and Cawse 1979, Sposito and Page 1984).

Pyrometallurgical processes employed in the production of Pb, Cu and Zn produce the largest emissions of atmospheric Cd, Cu and Zn (Pacyna 1989) and the second largest emissions of atmospheric Pb. Primary production of Cu, Pb and Zn accounts for $5.52 \times 10^3$ tonnes $yr^{-1}$ Cd, $22.75 \times 10^3$ tonnes $yr^{-1}$ Cu, $45.5 \times 10^3$ tonnes $yr^{-1}$ Pb and $70.73 \times 10^3$ tonnes $yr^{-1}$ Zn in world-wide emissions (Nriagu and Pacyna 1988). Equivalent emissions in Europe in 1982 were $0.73 \times 10^3$ tonnes Cd, $11.660 \times 10^3$ tonnes Pb, and $20.594 \times 10^3$ tonnes Zn (after Pacyna and Münch 1988, Pacyna 1988).

The field study sites in this thesis are located in close proximity to a base metal smelter at Avonmouth which is a major source of Zn, Pb and Cd contaminants within the area.

## 1.3. Introduction to the Study Area

Avonmouth is located on the east bank of the Severn Estuary immediately to the north of the mouth of the river Avon (Fig.1.3.1). The field study sites are two woodlands, called Hallen Wood (OS grid ref : ST 554 802) and Haw Wood (OS grid ref : ST 558 800), which lie 4.5km NE from the centre of Avonmouth at 60 metres (approx) above sea level upon an outlying southern extremity of the Tortworth Ridge. The area bordering the Severn Estuary to the north of the river Avon is a flat alluvial plain which forms the southernmost fringe of the Vale of Berkeley. This region is flanked to the east by a range of wooded hills and higher ground of which Hallen and Haw Woods are a part. The M5 motorway runs diagonally across the area from south-west to north-east bisecting Hallen Wood from Haw Wood.




Key:

= Woodland

= Relief > 60 metres O.D.

= Urban conurbation

= Hallen village

A = Hallen Wood

B = Haw Wood

C = Commonwealth smelter

D = Incinerator

Fig.1.3.1 The Avonmouth Study Area.

Bristol and Avonmouth form part of a large urban and industrial area; however Avonmouth, based at the mouth of the Avon, is best situated to receive imported bulk materials and therefore most of the major industrial work is carried out at Avonmouth rather than at Bristol. The major industries that have been established at Avonmouth include Norsk Hydro Fertilizers, ICI Severnside Chemicals, Butler's Chemicals, Sevalco Carbon Black, Severn Valley Brick Company, Bristol Chemicals and Commonwealth Smelting. Refuse disposal tips, Bristol sewage treatment works and the city incinerator are also located in the area.

Due to the variety of industrial concerns based at Avonmouth a mixture of aerial pollutants are released from the aforementioned sources. Substantial emissions of $SO_x$, $NO_x$ and carbon black occur, together with smaller emissions of arsenic, fluoride, ammonia and volatile organic chemicals. Sources of heavy metal release include major roads, incinerators, small metal plating and casting works and in the past the Portishead power station which has since closed down. However the major source of Zn, Pb and Cd emissions is from the Commonwealth Smelting Works owned by Pasminco Europe Smelting Division.

### 1.3.1. Atmospheric Emissions of Heavy Metals from the Avonmouth Smelter

The Commonwealth Smelter at Avonmouth is a primary lead/zinc base metal smelter 1.25km NE of the centre of Avonmouth and less than 1.5km from housing estates on the west side of Bristol at Lawrence Weston (Fig.1.3.1). The history of the Avonmouth smelter has been described by Cocks and Walters (1968). The smelter was first commissioned for zinc production in 1928/1929. Successive Zn producing processes have included Horizontal Retort distillation, a Vertical Retort process and, as at present, the Imperial Smelting Blast Furnace (ISF). In the retort techniques, the process gases are less efficiently scrubbed than they are in the ISF technique, such that emissions of a trace metal such as Cd may be 4-5 times higher for the retort techniques than for the ISF (Pacyna 1989). It was at Avonmouth that the revolutionary Imperial Smelting Process was developed which provides simultaneous smelting production of both zinc and lead. ISF production commenced in 1958, and in 1968 production was transferred to a new furnace (No. 4) as part of an extensive modernization scheme. Also included in the new expansion scheme were a cadmium plant, sulphuric and phosphoric acid plants, and an

**Table 1.3.1 Emissions from Avonmouth Smelter after Installation of a Venturi Scrubber**

| | Emissions (kg/hr) | | | | |
|---|---|---|---|---|---|
| Element | 1975 | 1976 | 1977 | 1984 | Emission Target |
| Cd | N.A. | <0.7 | <0.7 | 0.4 | 0.7 |
| Pb | 7.3 | 4.1 | N.A. | 4 | 5.4 |
| Zn | <8.2 | 4.5 | 6.0 | 6 | 11 |
| S | N.A. | N.A. | N.A. | 400 | N.A. |

S is emitted as $SO_3$.
Data from Health and Safety Executive (1975, 1976, 1977) and Coy (1984).

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effluent treatment plant. The annual production rate for which the smelter was designed is $90x10^3$ tonnes Zn, $40x10^3$ tonnes Pb, $0.6x10^3$ tonnes Cd, $200x10^3$ tonnes sulphuric acid and $75x10^3$ tonnes phosphoric acid (copper bullion is also produced at the plant). The Imperial Smelting furnace at Avonmouth is the only primary Zn smelter in the U.K. (Hutton and Symon 1987), and in the 1970's was the largest Pb/Zn smelter in the world.

It is inevitable that such a large-scale smelting concern will release emissions of heavy metals despite the use of scrubbers. Handling of ores and solid waste tips in and around the smelting complex are also bound to release metal particulates into the atmosphere. In 1975 a Venturi scrubber was installed in the smelter and output emissions have been monitored (Table 1.3.1). It has been estimated that annual stack emissions of Cd to the atmosphere are currently about 3.5 tonnes (Hutton and Symon 1987). Based on that rate of Cd emission, then it follows that Pb and Zn emissions are 35 tonnes and 52.6 tonnes per annum respectively.

Heavy metal oxides appear to form an important part of the atmospheric emissions from a point source such as the Avonmouth smelter (Allen *et al.* 1974). The following phases in emissions from the Avonmouth smelter have been identified: $PbSO_4$, $PbO.PbSO_4$, PbO, Pb, ZnO, alpha-ZnS and CdO (Harrison and Williams 1983). $SO_3$ is the main gaseous emission from the sulphuric acid plant at the Avonmouth smelter (Coy 1984).

The emission source, particle size and density, transportation changes in particle size and composition, and wind strength and direction are some of the factors that should be considered in atmospheric dispersion of heavy metal contaminants from a continuous point source such as a smelter stack (Davies

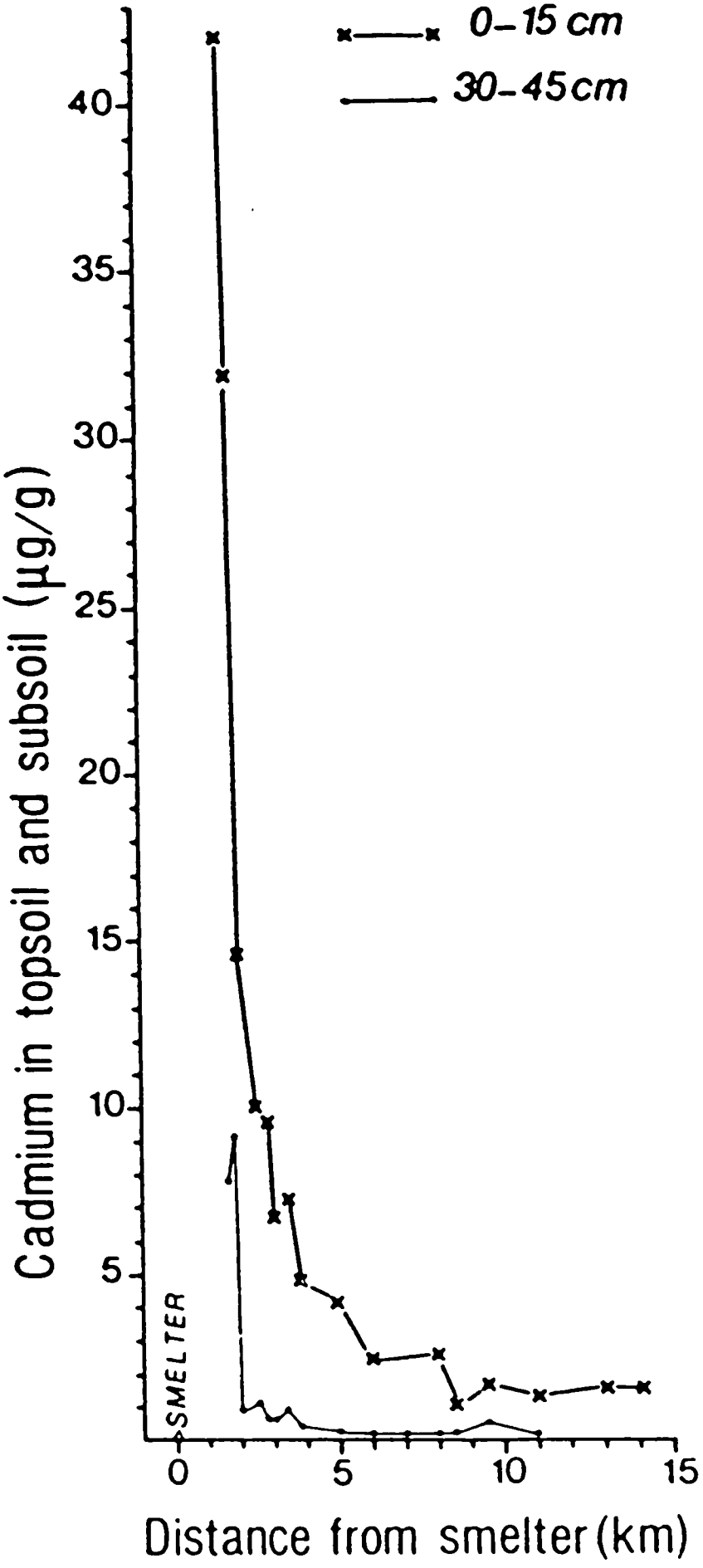


Fig.1.3.2 Cadmium in surface (0-15cm) and subsoils (30-45cm) downwind from the zinc-lead smelter at Avonmouth (after Marples and Thornton 1980).

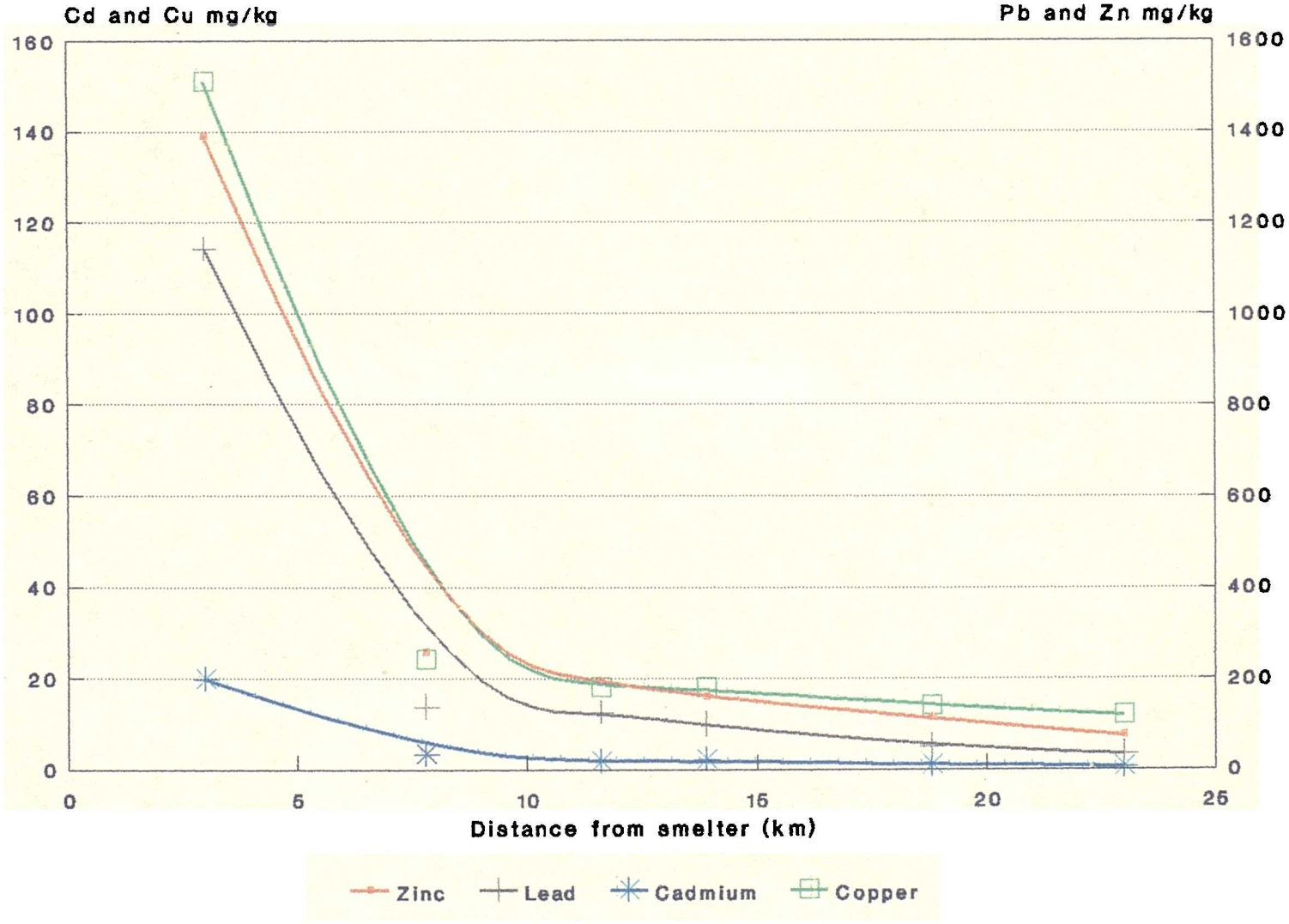


**Fig.1.3.3 Heavy Metals in Woodland Leaf Litter Downwind of the Avonmouth Smelter (data from Read et al. 1986)**

1983a). Heavy metal emitting stacks at Avonmouth are 50-60 metres high (Harrison and Williams 1983) and are comparable to the relative height of the study sites at 60 metres O.D. (Fig.1.3.1). The dominant winds blow from the west and south-west (Burkitt *et al.*1972, Little and Martin 1972) so that there is a strong directional component in the heavy metal distribution pattern around the Avonmouth smelter associated with the prevailing wind (Cameron and Nickless 1977, Gill *et al.*1975). The field study sites lie 3km downwind (east-north-east) of the Avonmouth smelter.

Deposition velocities of heavy metal particulates vary with particle size distribution, ground cover, and meteorological conditions (Sposito and Page 1984). Harrison and Williams (1983) found that the dominant west-south-west winds at Avonmouth did not produce higher deposition rates, and found (during the period of study) that dry deposition was a substantial proportion of the combined wet and dry deposition. Most of the particulate Pb, Zn and Cd should be less than 10μm in size (Allen *et al.* 1974). The mass median diameters (MMD) for Cd, Pb and Zn have been found to be between 0.8-2.5μm 700 metres ENE of the smelter, whereas at 1700 metres ENE finer particles for all three metals predominate (Harrison and Williams 1983).

The area surrounding a smelter often has severe metal contamination of soils and vegetation which decline exponentially to background levels at more distant sites (Freedman and Hutchinson 1981, Jones and Jarvis 1981). Such a pattern in the distribution of contaminants downwind of the Avonmouth smelter is illustrated in Fig.1.3.2 and Fig.1.3.3.

## 1.3.2. Description of the Field Study Area

The two study sites, Hallen and Haw Woods, are situated 2.9km and 3.1km respectively ENE of the smelter at Avonmouth. They are old oak-hazel (*Quercus robur, Corylus avellana*) woodlands with field layers which include *Hyacinthoides non-scripta, Milium effusum, Holcus lanatus* and *Mercurialis perennis*. The two sites occur on the first section of high ground to the NE of the Avonmouth smelter (Fig.1.3.1). The alluvial plain upon which the smelter is located has a base level height of approximately 6-7 metres O.D. which rises gradually to the village of Hallen at *circa* 15 metres O.D., after which the ground rises relatively steeply to more than 60 metres O.D. where both woods are located. The woodlands occur on a geological boundary where solid of Triassic age merges into solid of Jurassic age, such that there is a natural transition from the older Keuper marls through to Rhaetic beds (all Triassic in

age) to the eventual capping of younger Lias beds (Jurassic) with associated limestone bands.

As a result of the geology, soils are derived from the marls and clays of the parent materials so that heavy clay gleyed soils are a distinctive feature of the woodland sites. Soil Survey maps of the area suggest that the principal soil series covering the higher ground of Hallen and Haw Woods are the Denchworth and Worcester Series; the former series is associated with the Rhaetic and Liassic beds, whereas the latter is associated with the red marls of the Keuper beds. Merging boundaries of the Denchworth and Worcester Series bear some characteristics associated with soils of the Ham Series (Rhaetic/Lias head overlaying Keuper marl). The loamier/sandier topsoils of the Wedmore Series, subordinate soils of the Denchworth Series found on the northern outskirts of Bristol around Filton (approx. 3km east of Haw Wood - Fig.1.3.1), are not characteristic of the Hallen Wood and Haw Wood soils. The soils in the study areas relate reasonably well to the Hurcot Complex which covers the geologies and soils mentioned (for further details see Findlay 1976).

Soil material collected from Hallen and Haw Wood was principally derived from Rhaetic and Lias clays, although the lower third of the Hallen profile had hues (Munsell colours) more characteristic of Keuper marl derived soil (Table 1.3.2). The A and B horizons tended to be dominated by greyish brown to yellowish brown hues, although the Hallen profile had more of an olive grey hue in the B(g) horizon below 30cm depth. The first 10-11cm of topsoil was stained by organic matter and topped by L, F and H layers of woodland litter. The Haw leaf litter tended to have more highly decomposed litter in the H horizon than the Hallen leaf litter, that tended to contain more moderately decomposed leaf litter in the F (fermentation) horizon. Further details about the soils will emerge in the next Chapter. However, it should be mentioned that the slope, aspect and elevation where the Haw Wood profile was taken from are not too dissimilar to that of Hallen Wood.

Estimates of heavy metal deposition into Hallen Wood are given in Table 1.2.1. Previous studies have described the concentrations of metals in woodland plants and soils (Martin and Coughtrey 1981, Martin *et al.*1892), and in invertebrates (Coughtrey 1978, Hopkin and Martin 1982, 1983, Martin and Coughtrey 1976). Coughtrey *et al.* (1979) have shown that substantial accumulation of organic litter has occurred in heavily contaminated woodlands around the smelter. Martin and Coughtrey (1987) have mathematically modelled the movement of heavy metal contaminants in the top 31cm of Hallen Wood soil.

## Table 1.3.2 Description of the Hallen Soil Profile

Location : Hallen Wood, nr. Hallen (grid ref ST 554 802).

Slope & aspect : $20^{o}$ WNW.

Elevation : 60m O.D.

Land use : Woodland.

Horizons :

| cm | |
|---|---|
| 0-18 A | : Greyish brown (2.5Y 5/2) clay with yellowish brown (10YR 5/4-5/6) staining; some clay olive brown to light olive brown (2.5Y 4/4-5/6); soil moist; weak blocky structure; firm; roots abundant; merging boundary. |
| 18-30 B | : Yellowish brown (2.5Y 5/4-5/6) clay; increase of olive brown (2.5Y 4/4) and olive grey (5Y 6/2) with depth; mottles common, extremely fine - fine; distinct; common, very fine subrounded ferimanganiferous concretions; soil firm to plastic; weak blocky structure; moist; roots frequent/occasional; clear wavy boundary. |
| 30-55 B(g) | : Light olive grey (5Y 6/2) clay with increasing reddish brown (5YR 4/4) silty clay with depth at circa 45cm. Many fine, prominent, sharp mottles of yellowish brown (10YR 5/4-5/6) to olive yellow (2.5Y 6/6-7/6); common, fine, subrounded, ferrimanganiferous concretions. Soil firm to plastic; weak blocky structure; moist; roots occasional/rare; abrupt wavy boundary. |
| 55-65 BC | : Reddish brown (5YR 4/4) silty clay; soil very firm; moist weak blocky/massive structure; roots rare; merging boundary. |
| 65-84 Cca | : Reddish brown (5YR 4/4) silty clay; soil very firm; moist; massive structure; semi deformable; calcareous with crystals of calcium sulphate below 70cm depth. |

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## 1.4. Principal Aims of the Study

Our knowledge of the behaviour of polluting trace metals in soils is far from complete (Kabata-Pendias and Pendias 1984). The recognition of the associated environmental hazards connected with enrichment of toxic metals in the food chain and ground water is justification for many studies of the reactions of metals such as Cd, Cu, Pb and Zn with soils (Brümmer 1986). Knowledge of the mobility of heavy metals in forest soils is of great concern to environmental research (Bergkvist and Folkeson 1988), as is the loss of metals from the entire soil profile (Bergkvist *et al.*1989). In particular, the long term behaviour of such metals, their rates of migration in the soil profile and the chemical transformations that they undergo are important (Scokart *et al.*,1983). In terms of trace metal cycling and factors that enhance trace metal mobility, cadmium in particular is important because of its eminent toxicological importance (Förstner 1987).

In Hallen Wood and Haw Wood soils, the principal heavy metal pollutants are Cd, Pb and Zn. Mobility of Pb, Zn and Cd in the Hallen soil is considerably greater than that which would be inferred from existing literature and is probably the result of acid deposition in the study area (Martin and Coughtrey 1987). Mobilization of these metals will be influenced by their specific form which will ultimately determine the "behaviour" of their movement down the soil profile subject to the environmental processes at work in the study area. In view of this, the aims of this present study were to:

(a) Assess the degree to which heavy metals have moved down through woodland soil profiles subjected to the deposition of airborne heavy metals (Cd, Cu, Pb and Zn).
(b) Determine the solid phase heavy metals that are most readily available for movement down the soil profiles and/or are available for biological uptake.
(c) Determine the soil solution phase heavy metals, the solubility behaviour of which will determine mobility, leaching availability and toxicity of the metals in the soils.

Although both sites are located adjacent to one another (separated merely by the M5 motorway) and therefore possess similar ecological and pedological qualities, it is important to stress that:

(a) Hallen Wood appears to be more heavily contaminated with heavy metals than Haw Wood, probably accounted for by slight differences in exposure to the Avonmouth smelter.
(b) Soil metal profiles (Cd, Cu, Pb and Zn) appear to be developing at different rates in both woodland soils.

However, in view of the fact that the Haw Wood heavy metal soil profiles display similar concentration gradients to those recorded for the earliest Hallen Wood soil profile in 1975, it is felt that comparative studies of the soil profiles from these two woodlands are relevant in order to understand the features controlling the movement and bioavailability of Cd, Cu, Pb and Zn in these soils. The literature relevant to this study is covered at the beginning of each new chapter.

# CHAPTER 2

# HEAVY METAL POLLUTION IN SOILS

## Introduction

Physical, chemical and pedochemical weathering processes involving rocks exposed at the surface of the earth lead to soil formation; the principal factors of soil formation being expressed as:

$$\text{Soil} = f(Cl, O, R, P, T) \quad \text{(Jenny 1941)}$$

where:

| | | | |
|---|---|---|---|
| f | : function | R | : topography |
| Cl | : climate | P | : parent material |
| O | : biological activity | T | : time |

Such factors are responsible for soil profile development. Soil type will therefore depend on the factors that are most influential in pedogenesis. The behaviour of a heavy metal in a soil, whether derived from soil material through weathering or introduced as a contaminant, will depend on the heterogeneous mixture of organic and inorganic constituents that make up the biogeochemical soil system which is subject to pedogenic environmental processes.

## 2.1. Soil Constituents and Soil Processes affecting the Behaviour and Bioavailability of Heavy Metals in Soils

The fate of heavy metal inputs to the soil including their reactions and mobility within the soil (plus any subsequent uptake by plants) will be controlled by complex chemical reactions and a number of physical and biological factors (Jones and Jarvis 1981). As well as being retained in the soil solid phase, heavy metals are also present as free ions in the soil solution, present as soluble organo-mineral complexes and are adsorbed at the soil colloids (Cottenie 1980).

### 2.1.1. The Soil Solution

This constituent of the soil is covered in detail in Chapter 4, Section 1.

## 2.1.2. Solid Phase Precipitates

Many heavy metal ion concentrations in solution are controlled by the solubility of their metal hydroxides, sulphides or carbonates (Jørgensen and Jensen 1984). Although some attention has been given to the possibility that the concentrations of metal ions in the soil solution are controlled by precipitates of the metals as pure solid phases, in most situations in the soil, pure solid phases are not formed nor are the concentrations of the heavy metal ions normally high enough to exceed the solubility product (Jones and Jarvis 1981).

Co-precipitation, which occurs when a dissolved metal species is incorporated as a minor component in a solid phase as that phase itself is precipitated (Drever 1983), is perhaps a more important process. Mixed solid formation is a common process where dissolved primary minerals either reform or more often precipitate as secondary soil minerals such as clays or metal oxides (Table 2.1.1). The dissolution of primary minerals can in themselves release heavy metals that have been previously isomorphically substituted or included within them (Table 2.1.2).

However, precipitation of heavy metals, such as cadmium, can play an important role in controlling aqueous levels especially where natural waters are more alkaline (Pickering 1980), e.g. see Table 2.1.3. Furthermore, the surface effect of soil solids could concentrate ions at the solid-solution interface sufficiently to cause precipitation at a pH lower than that predicted from published solubility product data (e.g. Sillen and Martell 1964; Table 2.1.4).

## 2.1.3. Adsorption by Soil Surfaces: Soil Colloids

Adsorption is a process by which ions or compound substances are attracted to the surface of a solid. Colloids are substances of a very small particle size but have a large surface area to volume ratio. They usually possess surface charges and can be inorganic or organic in nature. The metal complexing functional groups exposed on inorganic solid soil surfaces include hydroxy groups protruding from the edge surfaces of layer silicates and from the surfaces of metal oxides, and also the ditrigonal cavities in the basal planes of clay minerals (Sposito and Page 1984). Some of the more important colloids with their typical charges are shown in Table 2.1.5. The negative charges fall into two categories:

## Table 2.1.1 Coprecipitated Trace Metals in Secondary Soil Minerals (after Sposito 1983)

| Mineral | Copreciptated |
|---|---|
| Fe Oxides | Cu, Zn, V, Mn, Ni, Mo |
| Mn Oxides | Zn, Pb, Fe, Co, Ni |
| Ca Carbonates | Cd, V, Mn, Fe, Co |
| Illites | Cu, Zn, Pb, V, Ni, Co, Cr |
| Smectites | Cu, Zn, Pb, Ti, V, Cr, Mn, Fe, Co, Ni |
| Vermiculites | Ti, Mn, Fe |

---

## Table 2.1.2 Modes of Occurrence of Heavy Metals in Primary Soil Minerals (after Sposito 1983)

| Metal | Occurrence in Primary Minerals |
|---|---|
| Cd | Sulphide inclusions and isomorphous substitution for Cu, Zn, Hg and Pb in sulphides |
| Cu | Sulphide inclusions in silicates; isomorphous substitution for Fe and Mg in olivines, pyroxenes, amphiboles and micas, and for Ca, K or Na in feldspars |
| Pb | Sulphide and phosphate inclusions; isomorphous substitution for K in feldspars and micas, for Ca in feldspars, pyroxenes and phosphates, and for Fe and Mn oxides. |
| Zn | Sulphide inclusions in silicates; isomorphous substitution for Mg and Fe in olivines, pyroxenes and amphiboles, and for Fe and Mn in oxides |

---

## Table 2.1.3 pH of Precipitation from a Synthetic Leachate Assuming Ionic Strength ≈ 0.1, $P_{CO_2} = 10^{-3.5}$ and Activity Coefficients of : Pb = 0.36; Zn = 0.4; Cu = 0.4; Cd = 0.4 (Newman and Ross 1985)

| Metal | Oxide | Hydroxide | Carbonate |
|---|---|---|---|
| Pb | 8.20 | 8.69 | 6.25 |
| Zn | 7.10 | 7.73 | 7.55 |
| Cu | 5.55 | 6.20 | 5.58* |
| Cd | 9.61 | 8.88 | 6.94 |

* : malachite

**Table 2.1.4 pH Values for Preciptation of Metal Hydroxy Species in the Presence of Suspended Solids (after Pickering 1980)**

| Nature of Suspension | pH* $Cd^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ | $Pb^{2+}$ | Reference |
|---|---|---|---|---|---|
| Kaolin | 7.2 | 6.8 | 6.1 | 5.9 | Farrah & Pickering (1978) |
| Illite | 7.3 | 6.6 | 5.8 | 5.9 | |
| Montmorillonite | 7.5 | 6.6 | 5.9 | 6.1 | |
| Cellulose | 6.9 | 6.8 | 6.4 | 6.0 | Farrah & Pickering (1978) |
| Hydrous Al Oxide | 6.6 | 5.6 | 4.8 | 5.2 | Kinneburgh *et al.*(1976) |
| Hydrous Fe Oxide | 5.8 | 5.4 | 4.4 | 3.1 | Kinneburgh *et al.*(1976) |
| Goethite, FeOOH | 7.7 | - | 5.2 | 5.6 | Forbes *et al.*(1976) |
| | 6.8 | | | | James *et al.*(1975) |
| $TiO_2$ | 6.0 | | | | James *et al.*(1975) |
| Hydrous Al Oxide | 6.6 | 5.6 | 4.8 | 5.2 | Kinneburgh *et al.*(1976) |
| Calculated from $pK_{SO}$ data | 8.8-9.8 | 7.4-8.5 | 6.1-6.9 | 6.1-9.1 | Sillen & Martell (1964) |

* : pH for 50% precipitation (±0.2) using an initial metal ion concentration of ≈ $10^{-4}$M

**Table 2.1.5 Charge Characteristics of Some Naturally Occurring Colloids (after Drever 1982, Plant and Raiswell 1983). N.A.=not available.**

| Colloid | Characteristic Charge | Isoelectric Points (pH) | Zero Point of Charge (pH) |
|---|---|---|---|
| Hydroxides and Hydrated Oxides : | | | |
| Silica | - | 1-2.5 | 2.0 |
| Aluminium Hydroxide/Oxide | + | 9 | 9.1 |
| Ferric Hydroxide/Oxide | Usually + (-) | 6-9 | 6.7-8.5 |
| Manganese Dioxide | - | 2 | 2-4.5 |
| Titanium Dioxide | + | 7.2 | N.A. |
| Zirconium Dioxide | + | N.A. | N.A. |
| Thorium Dioxide | + | N.A. | N.A. |
| Clay Colloids : | | | |
| Montmorillonite | - | <2.5 | 2.5 |
| Kaolinite | - (+) | 3.5 | 4.6 |
| Vermiculite | - | N.A. | N.A. |
| Illite | - | N.A. | N.A. |
| Sulphides | - | N.A. | N.A. |
| Carbonates/Calcite | Usually + | N.A. | 8-9.5 |
| Organic Colloids | - | N.A. | N.A. |

---

a) Permanent charges (more or less independent of pH) due to isomorphous substitution in the silicate framework and edge effects on clay minerals.

b) pH-dependent charges (variable charges) associated with reactions of protons at the surfaces of humic colloids, hydrous oxides and clay minerals (e.g. kaolinite).

The net surface charge of hydrous oxides and clay minerals, which contain hydroxyl groups, varies with pH. In acid solutions the surface charge becomes more positive, the cation exchange capacity (CEC) becomes smaller, and the anion exchange capacity (AEC) increases. In contrast in alkaline solutions, surfaces exhibit a more negative charge, CEC becomes significant and a decrease in AEC occurs (Drever 1982).

The pH at which the net surface charge is zero is known as the isoelectric point or zero point of charge (ZPC) and is determined by adsorption and desorption of protons alone (Table 2.1.5). Ultimately, the quantity and nature of colloids and surfaces within the soil (the solid phase) and nature and properties of the liquid phase will determine the CEC of the soil. Due to the greater number of negative charges on colloid surfaces (overall), the CEC in

soils exceeds the AEC. Heavy metals such as Cd, Cu, Pb and Zn naturally occur in soils as cationic species and hence the density of negative charges at the soil solid/soil solution interface will affect their adsorption.

Adsorption, however, can arise from electrostatic attraction alone, in which case it is relatively non-specific and non-selective, or from electostatic attraction augmented by hydrogen bonding or Loudon-van der Waal's bonding (Jørgensen and Jensen 1984). The former process characterises adsorption of ions by "cation exchange" onto surfaces (outer-sphere complexes) where the charged surface and diffuse cloud of oppositely charged ions (counterions) are referred to as a "double layer". Ions more or less attached to the solid surface form the "fixed" or "Stern layer", whereas ions further from the surface layer and more diffuse in the distribution form the "Gouy layer".

However, if covalent bonding augments electostatic attraction then specific adsorption occurs forming inner sphere complexes. The specific adsorption of metallic ions occurs most readily for metals that hydrolyse in water (e.g. Cd, Cu, Zn and Pb) and is pH dependent, i.e. increasing specific adsorption with increasing pH (Evans 1989). The pH of adsorption occurs somewhat below the pK (equilibrium constant) of the hydrolysis reaction of the metal in water such that the order of specific adsorption for soil minerals is as shown below (Brümmer 1986):

Affinity for adsorption : Pb > Cu > Zn > Cd

pK (Equilibrium constant)

| | Pb | Cu | Zn | Cd |
|---|---|---|---|---|
| Sillen & Martell (1964) | 7.8-7.9 | 7.3-8.0 | 9.0-9.4 | 7.6-11.6 |
| Brümmer (1986) | 7.7 | 7.7 | 9.0 | 10.1 |
| Baes & Messmer (1976) | 6.2 | 8.0 | 9.0 | 10.1 |
| Perrin (1969) | 8.0 | 8.0 | 9.0 | 10.1 |

Ionic radii unhydrated (nm)

| Pb | Cu | Zn | Cd |
|---|---|---|---|
| 0.12 | 0.072 | 0.074 | 0.097 |

The above illustrates that the specific adsorption of the metals increases with the increasing ability of the metals to form hydroxy complexes (taking ionic size into consideration).

Specific adsorption is not only restricted to surface sites, but also includes the internal lattice of the solid phase structure within iron oxides, manganese oxides, illites, smectites and other minerals into which heavy metals are able to enter via diffusion (Brümmer 1986). Under certain circumstances, co-precipitation may also involve adsorption (Sposito 1983).

Important metal-complexing functional groups that occur on the surfaces of soil organic matter are carboxyl, amine, and phenolic hydroxyl groups (Sposito and Page 1984). All the adsorptive sites on organic colloids are pH dependent. As well as being involved in cation exchange, humic substances can also be involved in an organic complexation process called chelation in which carboxyl groups of humic and fulvic acids play a predominant role (Alloway 1990). Beckwith (1959) suggested that the order of stabilities of different organo-metal complexes on humic substances should follow that of the series of Irving-Williams (1948) where:

$$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$$

For chelation to occur, the organic ligand must contain at least two donor atoms capable of bonding to the same metal ion and positioned within the ligand so that the formation of a ring (co-ordination complex) is sterically possible (Evans 1989).

### 2.1.4. Some Principal Soil Constituents: Clay Minerals, Oxides and Organic Matter

The most important chemical processes affecting the behaviour and bioavailability of metals in soils are those concerned with the adsorption of metals via non-specific adsorption (cation exchange), specific adsorption, organic complexation and co-precipitation (Alloway 1990). Sposito and Page (1984) suggested that:

a) Soils whose clay fraction is dominated by 2:1 layer silicates, metal cation adsorption should involve principally both inner and outer sphere complexes with siloxane ditrigonal cavities, although highly selective

adsorption by bivalent metals may occur through complexes with edge surface hydroxyl groups.

b) Soils whose clay fraction is dominated by 1:1 layer silicates and hydrous oxides, metal cation adsorption should involve the formation of hydroxy polymer coatings whose extent of surface coverage will depend sensitively upon the Lewis acid strength (i e. ionic potential) of the metal cation as well as the soil solution pH values.

c) Soils where organic surfaces are important to metal adsorption, both surface complexation by organic functional groups and hydroxy polymer formation are involved.

Clay minerals which occur in soils are shown in Fig.2.1.1. The five groups which are most common to soils are outlined in Table 2.1.6 and are found in soils derived from Lower Lias and Red Keuper Marl clays such as those at the Hallen and Haw Wood study sites - illite and montmorillonite being the important constituents in Denchworth/Worcester soils (Findlay 1976). The CEC of these clays takes on the following order of magnitude:

Montmorillonite, Vermiculite > Illite, Chlorite > Kaolinite > Halloysite

Consequently, the greater the CEC, the greater the ability of the clay to bind the metal ions (Kabata-Pendias and Pendias 1984). However, cation exchange rates tend to follow the order:

Kaolinite > Montmorillonite » Illite (Pickering 1980)

At low pH values (pH < 5), kaolinite can become positively charged and adsorb anions (Sposito and Page 1984). Clay mineral adsorbents show selectivity sequences for the metals Cd, Cu, Pb and Zn (Table 2.1.7). The general consensus for the range of conditions covered in the reports of Table 2.1.7 would suggest that Cu and Pb are preferentially adsorbed with respect to Cd and Zn. The adsorption of lead ($Pb^{2+}$) has been shown to be favoured by a factor of 2 or 3 over cadmium ($Cd^{2+}$) on montmorillonite, illite and kaolinite over a range of exchange saturation of about 5-95% (Bittell and Miller 1974). The tendency for the adsorption of Pb to be favoured in relation to Cu and Zn may be due to the Pb ion being considerably larger and more weakly hydrated than the first series transition metals (Cu and Zn). Consequently, adsorption of Pb would be favoured as it would be able to approach the negatively charged clay surfaces more closely than the more

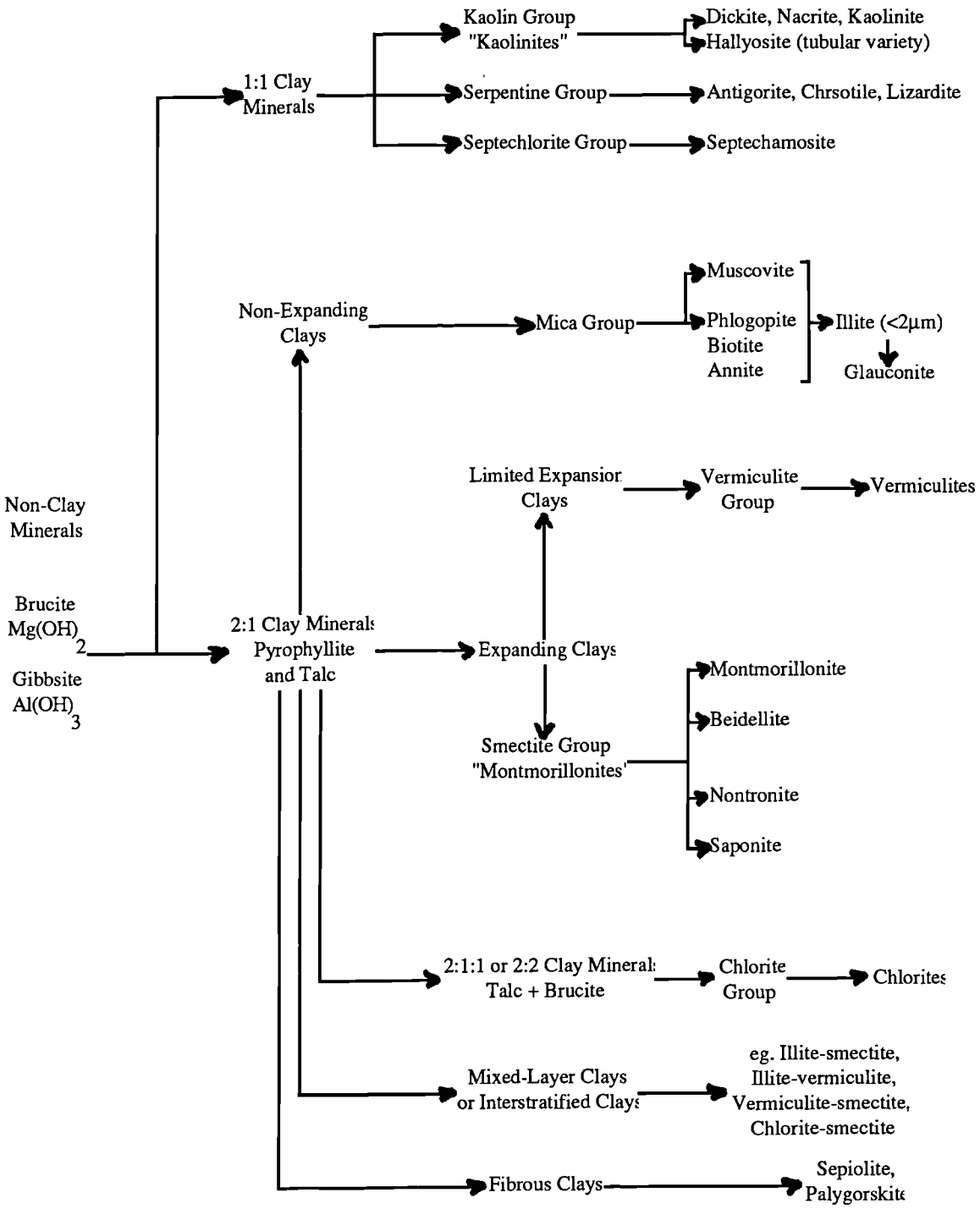



Fig.2.1.1 The Genealogy of Clay Minerals.

## Table 2.1.6 Comparative Properties of Four Major Types of Silicate Clay Found in Hallen Wood and Haw Wood Soils

| Property | 2:1 or 2:2 Chlorite | 2:1 Smectite (Montmorillonite) | 2:1 Fine Mica (Illite) | 1:1 Kaolinite (Kaolin) |
|---|---|---|---|---|
| Size (μm) | ) | 0.01-1.0 | 0.1-2.0 | 0.1-5.0 |
| Shape | | Irregular flakes | Irregular flakes | Hexagonal crystals |
| Specific Surface ($m_2/g$) | | 700-800 | 100-120 | 5-20 |
| External Surface | Similar to | High | Medium | Low |
| Internal Surface | Illite | Very High | Low | None |
| Cohesion, Plasticity | | High | Medium | Low |
| Swelling Capacity | | High | Medium | Low |
| Cation-Exchange Capacity (cmol/kg) | ] sheets | 80-120 | 15-40 | 3-10 |
| Interlayer Positions | $Mg(OH)_2$ $Al(OH)_2$ | (Exchange cations)$^{1}/_{3}$ + $H_2O$ | $K_1^+$ (fixed) | None |
| Tetrahedral Positions | $Si_4$ to $Si_2Al_2$ | $Si_4$ (some Al in some varieties) | $Si_3Al$ | Si, Al (septechlorite) $Si_2$ |
| Octahedral Positions | Mg, Al, Fe | Al, $Fe^{2+}$, $Fe^{3+}$, Mg $(Mg, Fe)_3$ biotite | $Al_2$ Fe, Al, Mg (septechlorite) | Al (kaolin), Mg (serpentine) |
| Thickness of Unit Layer | 14Å | Varies with $H_2O$ content. Commonly 14Å. Expands to 17Å with glyed | 10Å | 7Å |
| Simplest Formula | $Mg_6Si_4O_{10}(OH)_8$ (chlorite) | $Na_{1/3}Al_{2/3}Mg_{1/3}Si_4O_{10}(CH)_2$ (montmorillonite) | $KAl_3Si_3O_{10}(OH)_2$ (muscovite) | $Al_2Si_2O_5(OH)_4$ (kaolin) |
| Charge per Unit Formula | -1.1 | -0.4 | -0.8 | 0 |

Vermiculite is very similar to smectite, but with (exchange cations)$^{2}/_{3}$ ie. more interlayer cations to balance the higher electrostatic charge on the silicate framework (due to more substitution of Al for Si in the tetrahedral sheet). This, combined with more water in the interlayer space creates more charge per unit formula (-0.7) than smectite clays, but reduces vermiculites expansive properties (a limited expansion clay).

**Table 2.1.7 The Selectivity of Clay Colloids for Heavy Metals**

| Adsorbent | Selectivity Order | Reference |
|---|---|---|
| Kaolinite | Pb > Cu > Zn > Cd | Bittell & Miller (1974) |
| Kaolinite | Zn > Cd | Stuanes (1976) |
| Kaolinite | Zn > Pb ≥ Cu > Cd | Farrah & Pickering (1977) |
| Kaolinite | Cu, Pb > Cd > Zn | Farrah & Pickering (1978) |
| Kaolinite | Cd > Zn | Pulls & Bohn (1988) |
| Vermiculite | Zn > Cd | Stuanes (1976) |
| Montmorillonite | Pb > Cu > Cd > Zn | Bittel & Miller (1974) |
| Montmorillonite | Zn > Cd | Stuanes (1976) |
| Montmorillonite | Pb ≥ Cu > Zn > Cd | Farrah & Pickering (1977) |
| Montmorillonite | Pb > Cu > Cd, Zn | Farrah & Pickering (1978) |
| Montmorillonite | Cd = Zn | Pulls & Bohn (1988) |
| Illite | Pb > Cu > Zn > Cd | Bittel & Miller (1974) |
| Illite | Pb ≥ Cu > Zn > Cd | Farrah & Pickering (1978) |
| Illite | Pb > Cu > Zn > Cd | Farrah & Pickering (1978) |
| Clay Minerals | Cu > Pb > Zn | Mitchell (1964, 1972) |
| 2:1 Clay Minerals | Zn > Cd | Tiller *et al.*(1984) |
| Kaolinite | Cu > Pb > Zn | Wakatsuki *et al.*(1975) |
| Other Minerals (zeolites) : | | |
| Albite and Labradorite | Zn > Cd | Stuanes (1976) |
| Na Silicate Zeolite | Cu > Pb > Zn > Cd | Reynolds (1935) |
| Ca/Na-Al Silicates | Pb > Cu » Cd > Zn | Schwuyer *et al.*(1976) |

---

strongly hydrated heavy metals, Zn and Cu. The preference of illite for Pb is probably due to the ionic radii of lead ($Pb^{2+}$) and potassium ($K^{+}$) being similar (Hildebrand and Blum 1975). Potassium occurs as a fixed interlayer component in micaceous clays and lead is also capable of replacing potassium in the montmorillonite lattice (Marshall 1949). Since the ionization potentials of Cu and Zn are quite similar (Cu: 2.71, Zn: 2.70), the different adsorption behaviour of these two elements can only be attributed to polarization effects and as $Cu^{2+}$ possesses an unpaired election in the 3d-orbitals and is therefore more strongly polarized than $Zn^{2+}$ (which has no unpaired 3d-electrons), the former ion exhibits a greater affinity to anionic sites (Förstner and Whittman 1979).

Selectivity of metal cations for adsorption is also affected by the Lewis hard-soft acid-base (HSAB) principle (see Chapter 4 for further details). Cd, Cu, Pb and Zn are all chalcophile metals and Lewis acids. $Cu^{2+}$, $Pb^{2+}$ and

$Zn^{2+}$ are "borderline" metals whereas $Cd^{2+}$ is a "soft" metal Lewis acid. Cd is closely associated with Zn in its geochemistry as both elements have similar ionic structures (Group IIb in the periodic table) and electronegativities (c.f. ionization potential) and both are strongly chalcophile:

| | Zinc | Cadmium |
|---|---|---|
| Electronegativity | 1.7 | 1.7 |
| alpha-polarisability | 0.29 | 1.09 |
| Ionic radius (nm) | 0.74 | 0.97 |

However, the figures shown above indicate that in relation to Zn, Cd has a greater ionic radius and higher polarisability which provides $Cd^{2+}$ with its inherent "softer" Lewis acid nature in relation to $Zn^{2+}$. Hence $Cd^{2+}$ will tend to be adsorbed by softer base surface sites in relation to $Zn^{2+}$ which will tend to prefer harder base surface sites. Therefore, as the hydroxy functional groups on the edge of kaolinite crystals are softer bases than the siloxane ditrigonal cavity adsorption sites on montmorillonite, $Cd^{2+}$ will have a preference for the former sites (Pulls and Bohn 1988). However, complexing ligands complicate the application of the HSAB principle (Alloway 1990), such that the formation of the Cd-chlorocomplex can reduce the amount of Cd adsorbed at a surface site (Kinniburgh *et al.*1976) and contribute to the mobilization of the heavy metal ion within the environment (Hahne and Kroontje 1973). A further factor to consider is that there can be a limited number of adsorption sites with a high Cd preference on clays (Haan and Zwerman 1976). Such factors as the aforementioned will affect the selectivity of an adsorbent for a particular metal.

Several oxide minerals such as silicon oxides, titanium oxides, aluminium oxides and hydroxides occur in soils but, in relation to trace metal behaviour, the most important are Fe and Mn oxides (Kabata-Pendias and Pendias 1984). These latter oxides show particularly strong affinities for trace metals which involve mechanisms of adsorption and coprecipitation (Förstner and Whittman 1979). The age, degree of crystallinity and hydration state of iron oxides affects the porosity and surface area (Crosby *et al.*1983) which in turn affects the adsorptive capacity of the metal oxide (Newman and Ross 1985). The capacity for adsorption by iron oxides is at least ten times less than manganese oxides (Jørgensen and Jensen 1984) and hydrous Mn oxides have extremely high adsorption capacities and high adsorption affinities for heavy metals (Drever 1982). Both Mn and Fe hydrous oxides are exceedingly fine grained, with surface areas of up to 2-300$m^2$/g. Mn oxides, however, have a CEC of up to 150 meq/100g (equivalent to those of vermiculite and montmorillonite) where

## Table 2.1.8 The Selectivity of Oxides for Heavy Metals

| Oxide | Selectivity Order | Reference |
|---|---|---|
| Fe Oxides : | | |
| Goethite | Cu > Zn | Grimme 1968 |
| Goethite | Cu > Pb > Zn > Cd | Forbes *et al.*(1974, 1976) |
| Goethite | Cu > Pb > Zn | McKenzie (1980) |
| Haematite | Pb > Cu > Zn | McKenzie (1980) |
| Amorphous Oxides | Pb > Cu > Zn > Cd | Kinniburgh *et al.*(1976) |
| Amorphous Oxides | Pb > Zn > Cd | Gadde & Laitinen (1974) |
| Hydrous Ferric Oxides | Zn > Cd | Kuo (1986) |
| Al Oxides : | | |
| Amorphous Oxides | Cd > Pb > Zn > Cd | Kinniburgh *et al.*(1976) |
| Silica Oxides : | | |
| Silica Gel | Cu > Zn > Cd | Dugger *et al.*(1964) |
| Silica Gel | Cu > Zn | Wakatsuki *et al.*(1974) |
| Silica Gel | Pb > Cu > Cd | Schindler *et al.*(1976) |
| Mn Oxides : | | |
| Hydrous Mn Oxides | Cd > Zn | Kozawa (1959) |
| Hydrous Mn Oxides | Pb > Zn > Cd | Gadde & Laitinen (1974) |
| Hydrous Mn Oxides | Cu > Zn | Murray (1975) |
| Various Mn Oxides | Cu > Zn | McKenzie (1970, 1972) |
| Various Mn Oxides | Pb > Cu > Zn | McKenzie (1980) |
| Fe/Mn Oxides : | | |
| | Pb ≥ Cu » Zn > Cd | Scheffer & Schachtschabel (1982) |

as the CEC of Fe oxides/hydroxides is much lower. However, unlike the negatively charged silicate clays such as vermiculite and montmorillonite, oxide surfaces may bear positive, negative or zero net charge depending on the solution pH.

Specific adsorption of heavy metals on oxides is of far more importance than cation exchange. The actual pH at which adsorption becomes pronounced depends partly on the tendency of the metal to hydrolyze and partly on the properties of the oxide surface. The selectivity of oxides for heavy metals Cd, Cu, Pb and Zn is illustrated in Table 2.1.8. Again, as for adsorption selectivity for metals on clays, under the conditions of experiment it would appear that Cu and Pb are more selectively adsorbed upon oxides than are Zn and Cd. Significant adsorption can still occur at the point of zero charge on oxides (eg. Murray 1975) indicating that specific chemical forces are involved in the adsorption process in addition to electrostatic forces (Drever 1982). Indeed, the high capacity of an oxide for metals such as Cu and Pb is inconsistent with a

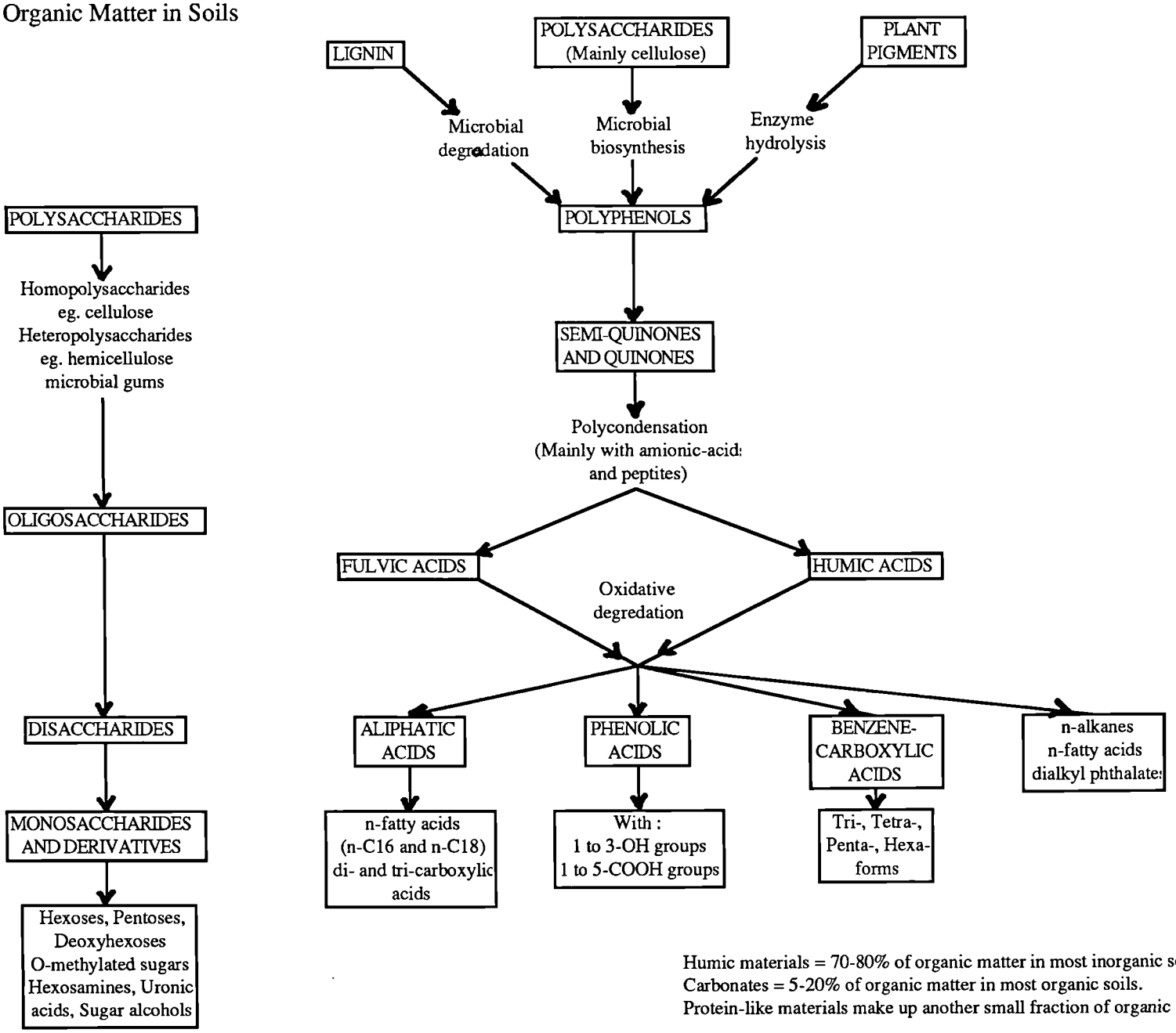
purely surface phenomenon and suggests that an open permeable structure exists within the oxide (Swallow *et al.*1980). The pK hydrolysis constants for Pb and Cu are quite similar and hence the position of Pb and Cu in the selectivity (Table 2.1.8) may alter. The hydrolysis constants (pK) given by Brümmer (1986) and Perrin (1969) are the same for Pb and Cu; hence Forbes *et al.* (1976) suggested that reversal in the selectivity order of Pb and Cu on goethite may be due to the higher interaction energy of the larger $Pb^{2+}$ ion. Adsorbents such as Fe oxides also act as hard Lewis bases, hence such surfaces will tend to preferentially adsorb $Zn^{2+}$ in relation to $Cd^{2+}$ (Pulls and Bohn 1988).

Some of the organic constituents to be found in soils are shown in Fig.2.1.2. Colloidal soil organic matter can be divided into non-humic and humic substances. Non-humic substances include amino acids, organic acids, carbohydrates, fats and waxes whereas humic substances are a group of acidic, yellow/black coloured polyelectrolytes of moderately high molecular weight. Humic substances constitute the bulk of the organic matter in soils, estimated at 70-80% of the organic matter in most soils (Schnitzer 1980, Schnitzer and Khan 1978). Humic substances are comprised of humin (alkali insoluble), humic acid (alkali soluble/acid insoluble) and fulvic acid (alkali and acid soluble). Their CEC s decease in the following order (Hayes and Swift 1978):

Humin > Humic Acid > Fulvic Acid

In the pH range between 4.5 and 8.5, the CEC of soil organic matter is much larger than the CEC of any inorganic solid phase in soil (Sposito and Page 1984). Some of the physical and chemical characteristics of humic and fulvic acids are given in Table 2.1.9. Humic materials contain, per unit weight, large numbers of oxygen-containing functional groups (-COOH, -OH phenolic, -C=O), through which they can attack and degrade soil minerals by complexing and dissolving metals and transporting these within soils (Schnitzer and Khan 1978). Humic substance/metal ion interactions involve ion-exchange, surface adsorption, chelation, coagulation and peptization reactions (Mortensen 1963). Low molecular weight organic ligands, not necessarily humic in origin, can form soluble complexes with metals so preventing the metals being adsorbed at other surfaces or being precipitated (Alloway 1990). Soil organic matter has been of particular interest in studies of heavy metal retention in soils because of its significant impact on CEC, its involvement in buffering soil pH and, more importantly, the tendency of transition metal

Fig 1.2 Organic Matter in Soils




Humic materials = 70-80% of organic matter in most inorganic soils.
Carbonates = 5-20% of organic matter in most organic soils.
Protein-like materials make up another small fraction of organic materials

**Table 2.1.9 Physical and Chemical Properties of Humic and Fulvic Acids (after Snoeyink and Jenkins 1980)**

| Property | | Humic Acids | Fulvic Acids |
|---|---|---|---|
| Elemental Composition (% by weight) | | | |
| | C | 50-60 | 40-50 |
| | H | 4-6 | 4-6 |
| | O | 30-35 | 44-50 |
| | N | 2-4 | < 1-3 |
| | S | 1-2 | 0-2 |
| Solubility in Strong Acid (pH1) | | Not soluble | Soluble |
| Molecular Weight Range | | Few 100- Several million | 180-10000 |
| Functional Group Distribution | | Percent of oxygen in indicated functional group | |
| Carboxyl | —COOH | 14-45 | 58-65 |
| Phenol |  —OH | 10-38 | 9-19 |
| Alcohol | —C(—OH)— | 13-15 | 11-16 |
| Carbonyl | —C=O | 4-23 | 4-11 |
| Methoxyl | —O—$CH_3$ | 1-5 | 1-2 |

Dissociated carboxylic —COOH, enolic —C(—OH)—, and phenolic —OH groups are the major sources of negative charges.

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cations (e.g. Cd, Cu and Zn) and Pb to form stable complexes with organic ligands (Elliott *et al.*1986, Sposito and Page 1984).

Table 2.1.10 illustrates that the affinity for organic colloids to adsorb/complex Cu and Pb is greater than for Zn and Cd. Complexation with humic substances is important for hydrolyzable cations of heavy metals that form strong associations with oxygen and sulphur atoms such as $Cu^{2+}$ (Evans 1989). Sulphur containing groups (such at the thiol-SH group) found on organic colloids are particularly strong, soft Lewis bases that can form strong complexes with soft Lewis acids such as $Cd^{2+}$ (Evans 1989, Förstner and Wittman 1979). Scheffer and Schachtschabel (1982) suggested that the affinity for adsorption/complexation on humic substances was:

## Table 2.1.10 The Selectivity of Organic Matter for Heavy Metals

| Complexant/ Adsorbent | pH | Selectivity Order | Reference |
|---|---|---|---|
| Fulvic Acid | 3.5 | Cu > Pb > Zn | Schnitzer & Skinner (1967) |
| Fulvic Acid | 5.0 | Cu > Pb > Zn | Schnitzer & Skinner (1967) |
| Fulvic Acid | 5.0 | Cu > Pb > Zn | Schnitzer (1969) |
| Fulvic Acid | 3-5 | Cu > Pb > Zn | Schnitzer & Hansen (1970) |
| Fulvic Acid | 3-5 | Cu > Cd | Cheam & Gamble (1974) |
| Fulvic Acid | 4-9 | Pb ≥ Cu > Zn ≥ Cd | Schnitzer & Kerndorff (1981) |
| Humic Acid | Acid | Cu > Zn | Islam *et al.*(1970) |
| Humic Acid | 4-7 | Cu > Zn | Khana & Stevenson (1962) |
| Humic Acid | 3-7 | Cu > Zn | Khan (1969) |
| Humic Acid | 3-7 | Cu > Pb > Zn | Van Dijk (1971) |
| Humic Acid | ~7 | Cu > Zn | Stepanova (1974) |
| Humic Acid | 4-6 | Cu > Pb > Cd > Zn | Stevenson (1977) |
| Humic Acid | 2-6 | Pb ≥ Cu > Cd ≥ Zn | Kerndoff & Schnitzer (1980) |
| Humic and Fulvic Acid | | Cu > Pb > Zn | Jonasson (1977) |
| Peat | | Pb > Cu > Cd > Zn | Bunzl *et al.*(1976) |
| Organic Surfaces | Acid | Cd > Zn | Tiller *et al.*(1984) |
| Organic Surfaces | | Pb > Cu > Zn | Scheffer & Schachtschablel (1966) |
| Organic Complexes | | Cu > Pb > Zn | Jones & Jarvis (1981) |

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Fulvic Acid : Cu (4.00) = Pb (4.00) > Zn (3.60)
Humic Acid : Cu (8.65) > Pb (8.35) > Cd (6.25) > Zn (5.72)

The figures in parenthesis are stability constants (log K values) which show that the metals should form complexes more readily with humic acid than with fulvic acid. But in terms of metal mobilisation in soils, fulvic acids are the more soluble over a wide pH range (Cottenie 1980), but the solubility of fulvic acid-metal complexes is strongly controlled by the ratios FA/metal so that when the ratio is lower than 2, the formation of water-insoluble complexes is favoured (Kabata-Pendias and Pendias 1984). However, the lower the heavy metal content, the higher the energy linkage of the metallo-organic groups (Zunino *et al.*1979).

Guy and Chakrabarti (1975) established a general sequence of the capacity of solids to exchange/adsorb metal ions:

$MnO_2$ > Humic Acid > Iron Oxide > Clay Minerals

Other reports have also suggested similar sequences for the adsorption of Cd, Cu and Zn:

| Metal | Order | Reference |
|---|---|---|
| Cd | Fe or Al Hydrous Oxides > Humic Acid = Montmorillonite > Soil Clay | Pickering (1980) |
| Cd | $Al(OH)_3$ > $Fe(OH)_3$ > Montmorillonite > kaolinite | Chubin and Street (1981) |
| Zn | $\partial MnO_2$ > Al-oxide = Fe-Oxide > Humic Acid » Bentonite » $CaCO_3$ | Brümmer *et al.*(1983) |
| Cu | Organics > Fe/Mn Oxides » Clay Minerals | Adediran and Kramer (1987) |
| Cu | Mn oxides > Organics > Fe Oxides > Clay Minerals | Ure and Berrow (1982) |

Abd-Elfattah and Wada (1981) suggested that Fe-oxides and amorphous aluminosilicates (allophane and imogolite) are important adsorbents for Cd, Cu, Pb and Zn in terms of the higher proportion of selective adsorption sites that these adsorbents have:

Pb : Fe Oxide, Halloysite, Imogolite, Allophane > Humus, Kaolinite > Montmorillonite
Cu : Fe Oxide, Halloysite, Imogolite > Humus, Allophane, Kaolinite > Montmorillonite
Zn : Fe Oxide, Halloysite, Imogolite > Kaolinite > Allophane, Humus > Montmorillonite
Cd : Fe Oxide > Imogolite > Humus > Allophane, Kaolinite > Halloysite, Montmorillonite

Interestingly 1:1 layer silicates such as halloysite and kaolinite generally have a higher proportion of selective adsorption sites for the metals shown above in comparison to the 2:1 layer silicate montmorillonite. However, the CEC of the latter clay mineral is much larger than that of the 1:1 clay minerals, hence the capacity for metal adsorption on montmorillonite is much greater (see above: Pickering 1980 and Chubin and Street 1981 for Cd). Nevertheless, the adsorptive capacity of oxides and oxyhydroxides appears to be particularly important from the above sequences. Mn oxides can attain very high heavy metal adsorption capacities and, in the case of Pb, Mn oxides can adsorb up to 40 times more lead than Fe oxides (McKenzie 1980). The oxides ability to adsorb metals below the p.z.c. (Kuo and McNeal 1984) means that (at low pH) adsorption at these surfaces may be the dominant mechanism of heavy metal

immobilization, especially in the subsoil horizons (Cavallaro and McBride 1984). Tables 2.1.7, 2.1.8 and 2.1.10 suggest that the heavy metal affinity series for soil components is:

Pb, Cu > Zn, Cd

Such an order of selectivity agrees with what is known about the selectivity of adsorption of metals on a variety of soil constituents:

Pb, Cu > Zn > Cd (Abd-Elfattah and Wada 1981)

It is also in concordance with what is known about the natural order of metal complex stabilities (Irving and Williams 1948, 1953, Matthess 1984) and the ability of the metals to hydrolyse (Brümmer 1986) (see Section 2.1.3).

However, adsorption of heavy metals by various substrates is affected by a variety of factors such as the solution pH, the concentration of cation and substrate (Benjamin and Leckie 1981, Dzombak and Morel 1986, James and Healy 1972, Murray 1975), the nature of the substrate (Davies-Colley *et al.* 1984, James and McNaughton 1977, Tiller *et al.* 1984), the presence of competing ions (Benjamin and Leckie 1980, 1982, Christensen 1987a, 1987b, Gadde and Laitinen 1974, Tiller *et al.* 1979, Zasoski 1974) and of complexing ligands (Benjamin 1979, Davis and Leckie 1978, McNaughton and James 1974) and temperature (Johnson 1990). Also, within soil systems, interaction between soil constituents occurs. For example, humic substances can encourage the dissolution of other constituents such as oxides and clay minerals and can affect the adsorptive ability of other constituents by themselves adsorbing onto or within the other constituent (Schnitzer and Khan 1978; see also Curtis 1966). Nevertheless, a number of reports that have covered the adsorption of heavy metals on soil material suggest that Pb and Cu are more preferentially adsorbed than Zn and Cd (e.g. Cavallaro and McBride 1984, Harter 1983, Kuo and Baker 1980, Kurdi and Doner 1983) such that the relative retention and selective adsorption of metals by soils follows the order:

Pb > Cu > Zn > Cd (Elliot *et al.* 1986, King 1988 a)

But for soils with higher organic matter contents (between 20-48g OM per kg soil) the order may change where by:

Pb > Cu > Cd > Zn (Elliott *et al.*1986, King 1988 a)

Of all the soil components (oxides, organic matter and biota, carbonates, phosphates, sulphides, basic salts and clays) Kabata-Pendias and Pendias (1984) considered that clay minerals, hydrated metal oxides, and organic matter were the most important soil constituents in contributing to and competing for the sorption of trace metals. They further suggested that the ability of the solid phase to exchange cations, the CEC, was one of the most important soil properties governing the cycling of trace metals in the soil. Hence the amount of organic matter and clay in a soil can affect the bonding energy coefficients of the soils for heavy metals, such that the coefficients decrease in the order:

Organic Soils > Heavy Clay > Sandy and Silt Loam > Sandy Soil

(e.g. see Pickering 1980, Kiekens 1986 in Kiekens 1990, and Kiekens and Cottenie 1984 for sludge form soils).

Even though the amount of organic matter content of soils is usually much less than that of clay, it nevertheless makes a major contribution to the CEC of a soil because of its high adsorptive capacity at pH's above 5; CEC values of humic colloids being 150-300 meq/100g (Alloway 1990). However, although the CEC is widely used in regulations governing metal loading rates on agricultural land in the USA, constituents such as Fe oxides and clay content may be more suitable parameters for such assessments (King 1988 a). But, despite the importance of a particular constituent such as Fe and Mn oxides together with the overall CEC of a soil, the capacity for a soil to control the movement and availability of heavy metals will depend on other environmental factors: two particularly important soil factors being the soil pH and pE.

## 2.1.5. Soil pH and pE

### (A) Soil pH

The soil reaction is the pre-eminent factor controlling the chemical behaviour of metals and other important processes within the soil (Alloway 1990). Sposito (1983) discussed the importance of pH in relation to surface adsorption on mineral surfaces taking into account the model of James and Healy (1972) for oxide minerals. He suggested that this model takes into account several

**Table 2.1.11 Adsorption of Heavy Metals on Goethite as a Function of pH. (Data expressed as % of initial amount of ion in solution, after Quirk and Posner 1975)**

| Metal | pK (approx) | pH 4.7 | 5.2 | 5.5 | 5.9 | 6.4 | 7.2 | 7.5 | 8.0 |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 8.0 | 17 | 55 | 75 | 90 | - | - | - | - |
| Pb | 8.0 | - | 43 | 56 | 75 | - | - | - | - |
| Zn | 9.0 | - | - | - | 13 | 22 | 68 | - | - |
| Cd | 9.5 | - | - | - | - | 23 | 44 | 53 | - |

20 mg geothite / 40cm$^3$
Initial concentrations of metals (as chlorides) = 3.2 x $10^{-5}$M

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aspects of the experimental adsorption data as presented by a number of reports in Tables 2.1.7, 2.1.8, and 2.1.10:

a) pH strongly affects adsorption - adsorption being completed over a narrow range of one or two pH units.
b) Rapid increase in adsorption will occur at a certain pH value depending upon the trace metal. This is related to the first hydrolysis constant and the hydroxide solubility product constants for the trace metal (Kinniburgh *et al.*1976).
c) The pH range where the most rapid increase in adsorption occurs for the trace metal cation $M^{2+}$ the parameter log $[(M^{2+})(OH^-)]$ remains constant (Farrah and Pickering 1977) whereas the ion activity product $(M^{2+})(OH^-)^2$ does not remain constant.

Increase in pH raises $OH^-$ activity in solution which in turn will encourage the formation of heavy metal hydrolytic species and the production of hydroxy bridging sites on certain adsorbent surfaces. The effect of pH on the adsorption of heavy metals on geothite is shown in Table 2.1.11.

However, due to the heterogeneity of soils and the relatively small amount of solution in the soil pore space, the pH concept for this medium is not as precise as it is for solutions in vitro (Alloway 1990). Nevertheless, in acidic soils the adsorption reaction on inorganic colloids is largely reversible where at pH5.5 some of the heavy metals, eg. $Cd^{2+}$, are not much stronger competitors than $Ca^{2+}$ for adsorption sites. But as the pH rises above pH5.5 adsorption increases abruptly so that for many heavy metals the reaction is partly

irreversible (Jones and Jarvis 1981). As the pH values for soils decrease below pH5, desorption of metals such as $Cd^{2+}$ and $Zn^{2+}$ should become much more evident (Cottenie 1980). Brümmer (1986) suggested that, although ulterior factors have to be considered (such as soil water content, departures from equilibrium to non-equilibrium conditions, and the changes in activity of micro-organisms), pH is related to the reactions of heavy metals in soils such as precipitation-dissolution, adsorption-desorption, and complex and ion-pair formation. These in turn influence the distribution of the various metal species in the soil solution and solid phases.

## (B) Soil pE (Eh)

There are three main ways in which the pE value can produce indirect effects on the chemical forms of metals in soils (Sposito and Page 1984):

a) If the pE value falls below -2.0 (Eh < -120mV), $SO_4^{2+}$ can be transformed to $S^{2-}$. Consequently, the formation of metal sulphides could occur (Connel and Patrick 1968).
b) At low pE values, preservation or production of organic compounds could occur as a result of reducing conditions affecting the activity of microbes. Instead of degrading larger organic materials, production of organic acids is encouraged which may enhance complexation of metals.
c) Low pE values may solubilize Mn and Fe oxides. This is particularly encouraged when the pH value of the soil is low. Hence reduction can act to solubilize trace metals specifically adsorbed onto the $Fe^{3+}$ and $Mn^{4+}$ oxides and hydrous oxides (Reddy and Patrick 1983). As Fe/Mn oxides co-precipitate and adsorb significant amounts of trace metals in soils, the increase of trace metals in solution could be significant.

The resulting impact of Fe/Mn oxide reduction in soils to the soil chemistry is (see Ponnamperuma 1972):

a) An increase in water soluble $Fe^{2+}$ and $Mn^{2+}$.
b) An increase in pH.
c) A displacement of cations from the adsorption complex into the soil solution.
d) An increase in the solubility of P and Si.
e) The formation of new minerals.

Therefore in reducing soil conditions, the solubility of several heavy metals initially increases (Cottenie 1980). Long term flooding/waterlogging of soils could encourage the formation of sulphide precipitates.

The presence of ferrimanganiferous nodules and mottling features within the Hallen/Haw soils in this study suggest that redox reactions could affect metal mobility. Soils that form upon Triassic and Liassic clay types, upon which Hallen/Haw soils are found, generally can become seasonally waterlogged (Wetness Class III-IV). The importance of seasonal pH and pE changes in the Hallen/Haw soils is as yet unknown and would perhaps merit further study.

### 2.1.6. Soil Texture

This physical phenomena is related to matters that have already been discussed (e.g. adsorption, pH, pE and CEC). Clayey soils, such as those found in Hallen and Haw Wood are rich in layer silicates. Such clay particles are small in size with a greater surface area than that of the larger sand and silt fractions. 2:1 layer silicates, such as montmorillonite and vermiculite, can contribute a great deal to the CEC of soils. Clay soils tend to have high water holding capacities in relation to sandy or silty soils. The fine texture that a high clay content of a soil creates means that surface area, adsorbing power, swelling ability, plasticity and cohesion, and heat of wetting are all greater than would be found in sandier or siltier textured soils (Brady 1984). Fine textured soils with a high clay content can reduce vertical movement of water in relation to sandier soils. Hence, downward leaching rates may be affected in this way due to the lower saturated conductivities of the former soils. Furthermore, fine silt and clay can clog pores to produce a physical filtering effect. However, clay soils containing 2:1 expanding clay minerals such as montmorillonite will have the ability to shrink and expand as a result of drying or wetting respectively. Drying of such soils can lead to cracking of the surface soil which would encourage pedoturbative processes (Bridges and Davidson 1982, Johnson *et al.* 1987).

The silt / clay fraction of Denchworth or Worcester series soils, to which Hallen and Haw soils are affiliated, dominates the size class fraction for soil particulates. The clay fraction, however, appears to be the most dominant fraction especially for Denchworth clay soils (the percentage clay fraction generally being in excess of 50%; Findlay 1976). Clay soils are strongly buffered chemically (Bridges and Davidson 1982) especially if the soils contain high contents of 2:1 clay minerals such as montmorillonite or illite (see Brady

1984). In contrast, sandy soils have a lower buffer capacity (and low contents of iron and aluminium) which can make these soils susceptible to acidification and podzolization (Petersen 1980).

Soils that are rich in micaceous clays and montmorillonite have been found to be effective in reducing the mobility of metals such as Cd, Cu, Pb and Zn (Korte *et al.*1976). High clay content of such soils can help to reduce leachate flow rate and the migration of heavy metals through such soils (Alesii *et al.* 1980). However, the naturally higher pH of such soils should, perhaps, also be considered. The effective retention of trace metals such as Cu, Pb and Zn by the finer fractions of soils is illustrated by the tendency for trace metal enrichment within the silt/clay fractions of soils (Conner *et al.*1957, Fleming and Ryan 1964, Le Riche and Weir 1963, Shuman 1979, 1985).

### 2.1.7. The Adsorption Capacity of Soils

Soil characteristics which influence mobility of heavy metals such as Cd, Cu, Pb and Zn include pH, CEC, organic matter content, free-lime content, clay content, manganese, aluminium and iron oxide content, soil texture, redox potential and leaching rate (Martin and Coughtrey 1987). Such physical and chemical soil characteristics interact with the biological components of the soil to provide an environment in which a particular heavy metal will respond according to its physico-chemical nature. Such factors also constitute the matrix of individuality that gives a soil the ability to adsorb and buffer the input of heavy metal pollutants within a soil. The degree to which heavy metals are immobilized within soils depends primarily upon the capacity of the soil to retain the metals in an unavailable form (Allaway 1968, Jarvis 1977). Such a criterion will influence the uptake of more mobile heavy metals such as Cd and Zn in plants (e.g. McBride *et al.*1981, Kuo 1990a, 1990b) and affect the movement of such metals from surface contaminated soils to deeper uncontaminated horizons.

## 2.2. Heavy Metals in Soils and Forest/Woodland Litter

### 2.2.1. Heavy Metals in Forest/Woodland Litter

Smith (1981) suggested that there was substantial evidence to indicate that forest soils might be the ultimate or temporary repository for heavy metals associated with airborne particulates that were deposited within forest

**Table 2.2.1 Mean Concentrations of Heavy Metals μg/g (d.w) on Mature Oak Tree Leaves at Avonmouth (after Bewley 1980)**

| | Zinc | Lead | Cadmium |
|---|---|---|---|
| May | 430 | 350 | 0.8 |
| July | 1210 | 830 | 11 |
| September | 1120 | 1600 | 14 |
| November (leaves) | 1700 | 2600 | 37 |
| November (litter) | 1660 | 2500 | 35 |

---

ecosystems. Certainly, the greater proportion of the burden of heavy metals in forested ecosystems that are either fairly heavily contaminated or relatively unpolluted would appear to be contained within the litter and soil (Martin and Coughtrey 1987). In a number of ecosystems considered by Hughes (1981), soil was found to be the largest pool of Pb, Cu, Cd and Zn and litter usually the next largest pool. The importance of organic matter in litter and surface soils has been discussed by Hughes *et al.*(1980) who concurred with the view of Tyler (1972) that the characteristic localization of aerially deposited heavy metals near the soil surface was primarily related to organic matter accumulations at the soil surface. Often this results in Pb, Zn and Cd concentrations in the forest floor and in soil being related to organic matter content (Hughes 1981).

Where the surface soil is substantially polluted by atmospheric deposition of heavy metals, the surface few centimetres and especially surface organic materials may contain high total heavy metal concentrations compared with the original background contents of materials at greater soil depth (Brümmer 1986). The concentration of metals upon tree leaves close to source metal emissions increases with the seasonal age of the leaves (Table 2.2.1; see also Martin and Coughtrey 1981).

Hence forest organic surface layers (litter, fermentation and humus) often show an enrichment of heavy metals as a result of the air-filtering effect of the forest vegetation. As decomposition of litter proceeds heavy metal concentrations increase (e.g. Denaeyer-De Smet 1974, Martin and Coughtrey 1975, Tyler 1972) so that concentrations in surface organic layers can be greatest in the more decomposed fermentation (F/Oe/ or $O_2$) or humus (H/Oa/ or $O_3$) layers (eg. Friedland *et al.*1984 b, Jackson *et al* 1978, Smith and Siccama 1981, Strojan 1978a, Van Hook *et al.*1977, Watson 1975). This is illustrated

## Table 2.2.2 Concentration of Heavy Metals in Surface Organic Layers of a High and Low Contaminated Site

UK, Haw Wood litter profile (µg/g dry wt.)
Martin *et al.*1982

| | Cd | Pb | Zn | Cu |
|---|---|---|---|---|
| Litter | 6 | 293 | 644 | 44 |
| Fermentation | 22 | 1027 | 1450 | 67 |
| Humus | 52 | 1808 | 2349 | 88 |

Germany, Sachsen-Wald Forest litter profile (µg/g air dried)
Brümmer 1986

| | Cd | Pb | Zn | Cu |
|---|---|---|---|---|
| Litter | 0.8 | 135 | 67 | 91 |
| Fermentation | 1.6 | 220 | 85 | 104 |
| Humus | 3.0 | 240 | 99 | 57 |

---

in Table 2.2.2 where there is a tendency for metal concentration to be largest in the more decomposed organic fractions.

However in relatively uncontaminated sites, the trend is not very obvious and trace metal contents and concentrations are generally lower in the deepest increment of the forest floor (Moyse and Fernandez 1987).

Where higher levels of contamination occur, the standing crop of litter may be elevated at more polluted sites in relation to sites further away from the emission source eg. primary base metal smelting works (Coughtrey *et al.*1979, Strojan 1978a, Watson 1975). Litter accumulation in woodlands in the vicinity of the Avonmouth smelting works appears to be related to Cd and Zn concentrations in the litter (Coughtrey *et al.*1979). The absence of certain invertebrate groups (Hopkin *et al.*1985, Martin *et al.*1980) or the reduction of microbiological activity in contaminated litter probably account for increases in litter accumulation (Jordan and Lechavalier 1975, Strojan 1978 b). Comparison of litter quantities ($kg/m^2$) at a relatively uncontaminated oak/hazel woodland site at Wetmoor and two contaminated oak/hazel woodland sites at Haw and Hallen Woods (all within the vicinity of the Avonmouth smelting works) shows that substantial litter accumulation has occurred at the sites contaminated by heavy metals (see Table 2.2.3).

**Table 2.2.3 The Mean Quantities of Litter ($kg/m^2$) collected at three Woodland Sites in the Vicinity of the Avonmouth Smelter. N.A.=not available.**

| Year | Wetmoor | Haw | Hallen |
|---|---|---|---|
| 1977 | N.A. | N.A. | 8.34 |
| 1978 | N.A. | N.A. | 9.00 |
| 1979 | 0.91 | 7.91 | 11.96 |
| 1984 | N.A. | 7.90 | 14.15 |
| 1987 | N.A. | 8.21 | 12.35 |

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## 2.2.2. Soil Contamination and Mobility of Heavy Metals in Soils

The area surrounding a heavy metal point emission source such as a primary base metal smelting works will inevitably become contaminated with time (see Chapter 1). The degree of contamination in surface soils surrounding the pollutant source can be assessed from "background" metal concentrations measured for surface soils in the region prior to the first emissions from the pollutant source. However, such previous measurements of "background" levels are seldom available for the specific site of interest. In the case of the Avonmouth area, emissions of heavy metals from the smelting concern have been in progress since the late 1920's. Hence, the collection of soil heavy metal concentration data from relatively uncontaminated areas make a useful comparison with similar data collected from metal contaminated areas (Freedman and Hutchinson 1981).

Soil survey work in areas such as the British Isles helps to provide records of heavy metal concentrations in surface soils (e.g. Archer and Hodgson 1987, Davies 1983b, Reaves and Berrow 1984a, 1984b), although such work may also include soils that have been contaminated (e.g. from sewage sludges, or soils that include natural mineralizations). High levels of a metal such as Cd in the surface environment of England and Wales have been established by geochemical survey work by Webb *et al.*(1978). Thornton (1988), who made reference to such survey work, suggested that anomalous patterns of 4 mg/kg or more of Cd in stream sediment samples in the surface environment of England and Wales could be attributed to:

a) Cd associated with Zn ores in mineralised areas with associated mining and smelting (e.g. Shipham, Mendip in Somerset).

b) Cd (usually associated with Zn and/or Pb or other metals) dispersed by wind and water from industrial activities and large industrial conurbations.
c) Cd derived from natural mineralizations from black shales of the Carboniferous age (particularly in central and north west England).

With reference to those maps of Webb *et al.* (1978) which show the distribution of metals such as Cd and Pb in stream sediments over England and Wales (see also Howarth and Thornton 1983, Thornton and Plant 1980) it is clear that enhanced levels of such metals occur in the region of smelting works such as that located at Avonmouth (Marples and Thornton 1980). At Shipham, naturally high levels of heavy metals are associated with the parent dolomitic conglomerate in the area. Hence, soils derived from this parent material (Wrington Series) contain similar high levels of Cd, Pb and Zn. Neighbouring soil series, such as the soils of the Worcester Series developed on Keuper Marl, have also been affected by the mine working activities in the area such that surface horizons possess high levels of heavy metals such as Cd. However, the parent material of the Worcester Series soil at depth contain near "background" levels of Cd at 1mg/kg (for further details see Thornton 1988). Likewise, the previous example of Marples and Thornton (1980) in the Avonmouth area suggests that the background levels of Cd in the estuarine alluvium is circa 1-2 mg/kg at the soil surface and less than 0.5 mg/kg in the subsoil (Thornton 1981).

Table 2.2.4 illustrates the elemental composition of Cd, Cu, Pb and Zn in uncontaminated soils. Such figures have been derived from a large sample number: data being collected from an extensive review of literature. Kabata-Pendias and Pendias (1984) suggested that the range of mean metal concentrations for surface soils around the world are 0.06-1.1 mg/kg for Cd, 6-80 mg/kg for Cu, 10.4-84 mg/kg for Pb and 17-125 mg/kg for Zn. More recently, it has been proposed that the common values of metal concentrations in agricultural surface soils are:

| | | |
|---|---|---|
| Cd | 0.2-1 mg/kg | Alloway (1990) |
| Cu | 20-30 mg/kg | Baker (1990) |
| Pb | 10-30 mg/kg (rural)<br>30-100 mg/kg (urban) | Davies (1990) |
| Zn | 50 mg/kg | Kiekens (1990) after Lindsay (1972) |

## Table 2.2.4 Heavy Metal Composition of Typical Uncontaminated Soils

Metal Concentrations (mg/kg dry wt.)

| | Mean+ Soil | Mean* Soil | Median‡ Soil | Range+ Soil | Clarke Value |
|---|---|---|---|---|---|
| Cd | 0.06 | 0.62 | 0.35 | 0.01-0.7 | 0.2 |
| Cu | 20 | 25.8 | 30 | 2-100 | 55 |
| Pb | 10 | 29.2 | 35 | 2-200 | 12.5 |
| Zn | 50 | 59.8 | 90 | 10-300 | 70 |

+ : data from Bowen (1966) ‡ : data from Bowen (1979)
* : data from Ure and Berrow (1982)

Clarke value : mean concentration in Earth's crust

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In a survey by Archer and Hodgson (1987) of 1521 surface soils around England and Wales an assessment was made of the contents of heavy metals in surface soils based on clay or Keuper Marl lithologies:

Median Heavy Metal Contents (mg/kg)

| | Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| Clays | 0.3 | 17 | 33 | 84 |
| Keuper marls | 0.5 | 16 | 30 | 78 |

Such values as these might be regarded as suitable background values for the soils in this present study (at Hallen and Haw Wood sites) as they are associated with Denchworth and Worcester Series soil types that are derived from Liassic/Rhaetic clays and Keuper Marl parent materials.

Continuous contamination of a surface soil by above-ground inputs of heavy metals can eventually lead to substantial enhancement of metal concentrations in the top soil above what might be considered background or normal concentrations for that particular soil (e.g. Steinnes 1984, 1987). The persistence of contaminants in soils is much longer than in other components of the biosphere, and contamination of soil by heavy metals appears to be almost permanent (Kabata-Pendias and Pendias 1984). Once soils have become contaminated they are unlikely to be depleted of Pb and other metals by leaching (Davies 1983a). Therefore, regardless of their chemical forms, heavy metals that have been added to soils exhibit little mobility and even years after their

introduction, most of the added metals remain in the soil surface horizons (Chang *et al.*1984). Due to the capacity of soils to adsorb and immobilize heavy metals, soils have been used as filters to remove such metals from waste waters (Bouwer and Chaney 1974, Lehman and Wilson 1971).

Metals accumulated in soils are depleted slowly by deflation, erosion, plant uptake and leaching (Kabata-Pendias and Pendias 1984). Residence / depletion times of heavy metals in soils can be extremely long term (Allaway 1969). However, residence times of metals in soils depend largely upon the soil, degree of soil contamination and the conditions to which the soils are subjected (Bowen 1975, 1977, Enk 1983, Iimura *et al.*1977, Tyler 1978). The study made by Tyler (1978) for 10% depletion times of heavy metals in soils subjected to artificial acid rainwater leaching at pH4.2, 3.2 and 2.8 would suggest that depletion times for Cd and Zn were quite short especially under the most acidic conditions of pH2.8 water additions (< 2 years for 10% depletion in a control and polluted soil at pH3.2 and pH2.8 water conditions). In European heavily polluted soils, the time for 50% depletion of Cd was suggested as being between 2 and 11 years (Enk 1983).

Heavy metal movement down soil profiles and contamination of soil horizons at depth has therefore been a matter for consideration. Dowdy and Volk (1983) reviewed the literature for movement of heavy metals in soils associated with sewage sludge applications in column and field studies. They concluded that heavy metal movement would most likely occur with large sludge applications to sandy, acid, low organic matter soils which received high rainfall or irrigation; but even under such conditions the extent of metal movement would be limited. Nevertheless, movement of heavy metals has been reported in soils after additions of sludge / effluent: downward movement being recorded in coarse-textured (Lund *et al.*1976), loamy (Williams *et al.* 1980) and clay loam soils (Sidle *et al.* 1977; Sidle and Kardos 1977). Stevenson and Welch (1979) considered that as a heavy metal such as Pb was tightly bound by most soils, and since most investigations had shown that Pb was concentrated in the top few centimetres of soil after surface additions of the metal had occurred, then the general assumption could be made that Pb was immobile in soils and that little if any movement would occur beyond the surface deposition zone. However, they have reported, as have others (e g. Merry *et al.*1983) that Pb can migrate down soil profiles.

In their review of heavy metals in soils Kabata-Pendias and Pendias (1984) have suggested that:

a) Zn was considered to be readily soluble relative to other heavy metals in soils and that this metal was most readily mobile and available in acid light mineral soils such that losses of this metal could occur in podzols and brown acid soils derived from sands. Dowdy and Volk (1983) support this view as they concluded that in sewage sludge / effluent treated soils Zn was the heavy metal which most consistently had the potential to move in soils.
b) Cd, with respect to Zn, exhibited a higher mobility than Zn in acid environments such that Cd was most mobile in acidic soils within the range of pH4.5 to 5.5.
c) Cu was a rather immobile element in soils showing relatively little variation in total content in soil profiles, whereas Pb was reported to be the least mobile with respect to Cd, Cu and Zn.

From the literature reviewed by Martin and Coughtrey (1987) the general consensus was that Cd and Zn were relatively more mobile in soils than heavy metals such as Pb and Cu. Other studies not reviewed by the aforementioned authors agree that Pb and Cu are more immobile in soils with respect to Cd and Zn (e.g. Biddappa *et al.*1982, Gerritse and Van Driel 1984, Hickey and Kittrick 1984, Largerwerff *et al.*1976, Tyler and McBride 1982). Brümmer (1986) considered that the mobility of heavy metals in acidic soils decreased in the order:

$$Cd > Zn > Cu > Pb$$

The greater mobility of Cd and Zn in a variety of soils relative to Pb and Cu is further encouraged or enhanced when soils are subjected to acidification (e.g. Bergkvist 1986, 1987, Tyler 1981). The effect of artificial acid rainwater on polluted and non-polluted soils has shown that residence times for heavy metals such as Cd, Cu, Pb and Zn are reduced with a decrease in pH of precipitation water (Tyler 1978). Geochemical mobility of metals in soils subject to experimental leaching conditions is suggested as being:

$$Cd, Zn\ (high) > Cu > Pb\ (low)$$ (after Campbell *et al.*1983)

Soils affected by soil acidification release heavy metals to the soil solution; the effect being most pronounced for Zn and Cd (Jacks *et al.*1984).

Metal budget studies (principally for temperate forest ecosystems) have been reviewed by several authors (e.g. Bergkvist *et al.*1989, Hughes 1981, Kabata-Pendias and Pendias 1984). The most recent review by Bergkvist *et al.*(1989) indicated that metals such as Cu and Pb were associated with positive ecosystem budgets, whereas Cd and Zn in some examples were found to have negative ecosystem budgets. In the latter case, negative ecosystem budgets were associated with a larger output of Cd and Zn (g/ha/yr) from the deepest baseline from which the soil was sampled with respect to a smaller input of Cd and Zn (g/ha/yr) from atmospheric deposition. Smith (1981) regarded forest soils as important sinks for a variety of air contaminants, with the retention of particulate Pb by organic materials in the forest floor as a most dramatic example. He suggested that forest soils could act as less efficient sinks for other metals such as Cu, Cd and Zn when compared to Pb retention. However, he maintained that forest soil sinks were still important for such metals, particularly where the forest systems were close to primary source emissions.

High levels of total and extractable heavy metals have been recorded in surface soils in the vicinity of smelters (eg. Buchauer 1973, John *et al.*1975). High levels of total and extractable heavy metals found at depth in soils polluted by smelter emissions suggests that leaching and mobility of heavy metals can progress down soil profiles (e.g. Hazlett *et al.*1984, Scokart *et al.*1983). In this present study, at Hallen and Haw Wood, heavy metal movement has been recorded in soils over a period of time (over a period of 12 years at Hallen Wood).

## 2.3. Heavy Metal Movement down Soil Profiles at Hallen and Haw Wood

### 2.3.1. Introduction

The concern over heavy metal pollution within the environment has led to long term monitoring studies being carried out over a period of years within the vicinity of point source emitters such as smelting concerns, for example at Gusum in Sweden (Tyler 1984). Numerous reports have emerged of terrestrial contamination resulting from emissions from base metal smelters (e.g. see Freedman and Hutchinson 1981, Mattigod and Page 1983). Some particularly high levels of Cu, Pb, Zn and Cd pollution have been recorded in surface soils around such smelters (eg. Bolter *et al.*1972, Buchauer 1973, Hutchinson and Whitby 1973, Lagerwerff *et al.*1972). In addition to high total metal contents

occurring in such surface horizons of soil, high extractable metal contents (2.5% or 0.5 M HOAc extractable) of Cd, Cu, Pb and Zn have also been found (e.g. Goodman and Roberts 1971, Little and Martin 1972).

If soils are of a high pH (near neutral or alkaline) leaching of metals such as Cd, Cu, Pb and Zn from surface soils to depth is likely to be limited (e.g. Cartwright *et al.*1976). However, if substantial contamination of the surface soil has occurred, such metals may occur at elevated levels at depth (e.g. Buchauer 1973), and where high levels of metal contamination have occurred upon soils of a sandy consistency with an acidic reaction the mobility of heavy metals might be evident in the soil profile (Scokart *et al.*1983). There are a few, if any, studies (over a period of about a decade or more) that have examined the extent of heavy metal movement down soil profiles which have been aerially contaminated (Martin and Coughtrey 1987). In 1987, soil profiles were taken from the two aerially contaminated study sites, Hallen and Haw Wood, to ascertain the degree to which heavy metals (Cd, Cu, Pb and Zn) have moved down the woodland soil profiles since soil profile records were first taken in 1975 (Hallen Wood) and in 1979 (Haw Wood).

## 2.3.2. Materials and Methods

Since the mid 1970's, soil profiles have been taken from two aerially contaminated woodland sites in order to measure the concentrations of Cd, Cu, Pb and Zn. After digging a soil pit, samples of the organic woodland floor (L, F, and H) layers and the soil mineral layers were taken. The Litter (L), Fermentation (F) and Humus (H) layers were removed from a known area (30 x 15cm); these three layers being segregated from each other by the degree of organic matter decomposition. Then, once the organic layers were removed, apart from the top one centimetre of mineral soil, 2.5cm deep layers were collected in blocks. Due to the firm, plastic consistency of the soil, these slabby blocks were relatively easy to cut and remove as a unit. In the 1970's, profiles were collected to a depth of 31cm. During the 1980's, it was deemed necessary to sample to greater depths as the metal concentration profiles have altered with time. The Hallen 1987 soil profile has also been point sampled in a continuous vertical sampling line by taking soil cores every 2.5cm from the vertical face of the profile. Three vertical core profile lines were taken from the left, central and right side of the profile face each about 20cm apart horizontally.

The fresh soil samples were mixed and the pH of the fresh soils was assessed by glass electrode for each soil layer (using a 1:2.5 soil : deionised

water suspension). The soil was then allowed to air dry before being disaggregated and sieved (sieve mesh <= 2mm). Oven dry soil samples were used for loss on ignition at 375°C for 16 hours. Air dried soil was used to attain exchangeable bases, exchangeable hydrogen, CEC and percentage base saturation (after Brown 1943). Total metal concentrations were assessed by atomic absorption spectrophotometry (AAS) after wet acid digestion in concentrated Analar nitric acid. All metal concentrations are expressed on a dry weight of soil basis (mg/kg). For further details of AAS methods refer to Appendix A.

### 2.3.3. Results - Metal Movement and Redistribution down Woodland Soil Profiles

Due to the number of figures in this Section, Figs.2.3.1-2.3.14 have all been located at the end of this Chapter (pages 66-102). The soil profile metal concentration data to 46cm depth at the two woodland sites are shown in Figs.2.3.1, 2.3.2, 2.3.3 and 2.3.4 with the L, F, and H layers included. Also included are background concentration bars for the soil and organic litter layers. The background concentration for soil indicated in each figure has been based upon the maximum range value given by Bowen (1966) for Cu (100 mg/kg), Pb (200 mg/kg) and Zn (300 mg/kg). For Cd, the maximum range value of Thornton and Plant (1980) has been used at 2μg/g. Such values may be excessive for the Haw and Hallen Wood soils. However, they provide a useful baseline with which the movement of metals in the soil at the two woodland sites can be compared. Fig.2.3.5 shows the 1987 metal concentrations in comparison to soil background concentrations that are perhaps more representative for the woodland soils. Background organic litter concentrations in Figs.2.3.1-2.3.4 have been taken from an oak/hazel woodland 23km ENE of Avonmouth (see Coughtrey *et al.*1979, Read *et al.*1986).

In the Hallen profiles (1975-1987), Zn concentrations in the organic layers (L, F and H) have tended to decrease with time whilst, correspondingly, the Zn soil concentrations have increased with depth and with time (Fig.2.3.1). However, the Haw profiles (1979-1987) illustrate that the 1984-87 organic layer Zn concentrations have become enhanced with respect to the 1979 concentrations. Furthermore, the Haw soil Zn concentrations have maintained distinct concentration gradients similar to that of the Hallen 1975 profile. The organic layer Zn concentrations at both sites were considerably greater than background levels recorded at Wetmoor. If a soil Zn concentration of 300

mg/kg is taken as a background level, then at the Haw site Zn contamination would appear confined to the surface 16cm of soil whereas at Hallen Wood contamination of soil has occurred to a depth greater than 46cm. Fig.2.3.3 illustrates that Cd has responded in a similar fashion to Zn (see Fig.2.3.1). Note that the Haw 1985 Cd value for 13.5-16cm depth has been taken as the mean value between the values obtained for 11-13.5cm and 16-18.5cm depth. This has been done on account of the fact that the mean value of 9.9 mg/kg had excessive variance (the standard error being ±5.3). Figs.2.3.2 and 2.3.4 suggest that Pb and Cu concentrations tended to increase in the organic layers at both woodlands with time whilst soil concentrations were maintained at or below the background concentrations of 200 mg/kg for Pb and 100 mg/kg for Cu. The organic layer concentrations for Cu and Pb were greater than background metal levels (substantially so with respect to Pb).

In Fig.2.3.5 the Haw and Hallen profiles are shown in relation to background soil concentrations suggested by Archer and Hodgson (1987) for soils derived from parent clays and keuper marl. These median background concentration levels are not too dissimilar to the median concentrations provided by Bowen (1979) for Cd, Pb and Zn. Similarly, the mean background concentrations of Ure and Berrow (1982) for Cd, Pb (and perhaps Zn) bear a resemblance to Archer and Hodgsons' values. Hence, contamination of these soils to greater depth cannot be ruled out, and potentially contamination of the Hallen soil by Cd and Zn could have been as deep as 60cm or more. Furthermore, the concentrations of these two metals were substantially elevated in relation to such background levels (e.g. x 6 for Zn at 36cm depth and x 12 for Cd at the same depth) in the Hallen profile. Although Pb levels in Hallen Wood exceeded the 30-33 mg/kg background concentration (from Archer and Hodgson 1987) to 51cm depth, they were, nevertheless, quite normal for a soil in the sphere of influence of an urban conurbation (i.e. between 30-100 mg/kg Pb, after Davies 1990). However, the median background concentrations for Cu, suggested by Archer and Hodgson (1987) as being 16-17μg/g for soils derived from parent clays and keuper marl, appear to be too low for Hallen and Haw soils. Most of the Haw and Hallen profiles had Cu concentrations in the range of 16-35 mg/kg which conform more readily to the mean, median and range values suggested by Ure and Berrow (1982), Bowen (1979) and Baker (1990) respectively. However, the 1979 Haw Cu profile had Cu soil concentrations as high as 60 mg/kg. Even so, 60 mg/kg Cu is still within the background variation that may be expected within such soils. For example, the trace element content of Lower Lias clay collected from borehole material

demonstrates that the range of Cu in such material could vary between 7-95 mg/kg (Le Riche 1959).

Hence, overall, Cu and Pb concentrations in Haw and Hallen soil have conformed mostly to the concentrations normally found in British soils: 2-60 mg/kg for Cu and 10-150 mg/kg for Pb (Thornton 1981, 1983, Thornton and Plant 1980). Pb only exceeded 150 mg/kg in the surface layers of mineral soil at < 10cm depth. However, Haw and Hallen Cd and Zn soil concentrations were excessive with respect to the concentrations normally found in British soils (i.e. 1-2mg/kg Cd and 25-200 mg/kg Zn (Thornton 1981, 1983, Thornton and Plant 1980).

Fig.2.3.6 illustrates the results of the 1987 core profiles. Essentially, Figs.2.3.6b and 2.3.6d show that whilst there was spatial variation of Pb and Cu concentrations in the Hallen profile, as a whole, the main form of the their Hallen concentration profiles (as shown in Figs.2.3.5b and 2.3.5d) was still reasonably well maintained. The same seems true for Cd and Zn when Figs.2.3.6a and 2.3.6c are compared with Figs.2.3.5a and 2.3.5c. Comparison of the Hallen 1987 Zn profiles (Figs.2.3.5a and 2.3.6a) illustrates that whilst the main "wave" feature of Zn was characteristic of the Hallen soil, there was, nevertheless, some spatial variation in the vertical as well as the horizontal plane.

Figs.2.3.7a-c demonstrate the data available for the principal heavy metal pollutants Cd, Pb and Zn at Hallen Wood (1975, 1979, 1983, 1984, 1985 and 1987 profiles). These diagrams portray more lucidly the decline of Cd and Zn concentrations in the organic litter layers whilst a "wave" of Cd and Zn has progressed down the Hallen profile with time. However, whilst showing a general increase in the contamination of the organic litter layers, Pb shows no clear sign of movement down the Hallen profile with time. Figs.2.3.8-2.3.11 show the proportional distribution of Cd, Cu Pb and Zn down the Haw and Hallen Wood profiles with time. All the metal concentrations have been transformed to a percentage of total metal in each layer of mineral soil (i.e. 0-1cm, 1-3.5cm, 3.5-6cm etc.). This has been achieved by converting the metal concentrations to $mg/m^2$ using the formula:

$$\frac{\text{Metal Concentration (mg/kg)} \times 10000 \times \text{Soil Bulk Density} \times \text{Depth of Layer (cm)}}{1000}$$

The bulk density of the soils was established by using percentage loss on ignition readings at 375°C and converting them to bulk density using the conversion for forest soils (after Honeysett and Ratowsky 1989):

$$\frac{1}{\text{Bulk Density}} = 0.564 + (0.0556 \times \%\text{LOI at } 375^{\circ}\text{C})$$

The quantity of metals ($mg/m^2$) in Haw and Hallen soils for each year was calculated to 46cm depth as bulk profile sampling for Hallen 1984, 1985, 1987 and Haw 1985, 1987 profiles extended to this depth. Hallen 1975, 1979 and Haw 1979, 1984 profiles were only bulk sampled to 31-36cm depth. Therefore, in the case of these latter profiles, a natural concentration continuum line was taken in the assessment of missing concentration values to 46cm depth. For the Hallen 1975 and Haw 1979/1984 profiles this does not prove to be so difficult as background concentrations of the heavy metals have generally already been reached at 31cm+ depths. However, the continuation lines of the Hallen 1979 metal concentrations for Cd and Zn were perhaps a little more subjective as background concentrations had not been reached at 36cm depth. Nevertheless, further progression of the Hallen 1979 profile in the last 10cm of soil depth to 46cm has been made by using figures from the Hallen 1987 profile. The values used appeared to be naturally sequential to the Hallen 1979 data.

The results of the percentage distribution of metals in the soil profiles, as shown in Figs.2.3.8-2.3.11, help to normalize the data of successive profile years. These in turn help to elucidate the notion of whether heavy metal movement has or has not occurred down Haw or Hallen profiles. However, presentation of the data in this way may have its drawbacks. For example, in Fig.2.3.9b where the Hallen 1984 Pb profile had exceptionally low background Pb concentrations at depth (of < 1 mg/kg in some layers), the percentage Pb metal contents in the surface soil layers might have been over compensated for with respect to the Pb distribution in previous years. But Fig.2.3.11a demonstrates that the percentage distribution of Cu for all Haw profile years was similar despite the naturally higher background Cu concentrations of the 1979 profile (see Fig.2.3.4a).

Fig.2.3.11 illustrates that the Cu distribution for both woodland locations and for all profile years conformed to a relatively similar distribution pattern: the general trend (with increasing depth) being positive from about 1.5-2.5% at 0-1cm to about 6.5-7.5% at 43.5-46cm. There would appear to have been no major redistribution of the metal in the soil profiles with time (when compared to the earliest recorded profiles). The Cu peak in the Hallen 1984 profile at 6-8.5cm depth appears to be a single profile anomaly that occurred for that profile

year. All the Cu concentrations in the woodland soils were at 60 mg/kg or less; these concentrations are quite normal for British soils (eg. see Thornton and Plant 1980). Therefore no obvious signs of Cu metal movement down the Haw and Hallen Wood profiles are apparent.

Similarly, no major redistribution of Pb content with time down the soil profiles is apparent in Fig.2.3.9. However, the percentage distribution of Pb was enhanced within the top 11cm of both soils indicating some superficial movement of the heavy metal. However, the Pb concentrations at depths > 11cm corresponded to values that are considered normal for soils in the vicinity of an urban environment (i.e.values of <= 100 mg/kg - see Davies 1990).

Figs.2.3.8 and 2.3.10 for Zn and Cd show that whilst the % metal distributions in the Haw profiles remained relatively similar with time, the % metal distributions in the Hallen profiles, however, have undergone redistribution with time. The enhanced distribution of the Haw profiles in the topsoil reflects the distribution of the earliest Hallen 1975 profile. Movement of Cd and Zn, though, has occurred to depth in the Hallen soil with time, with the concentrations of Cd and Zn exceeding the maximum soil background concentrations given by Bowen (1966) and Thornton and Plant (1980) (see Figs.2.3.1 and 2.3.3).

The burden of the heavy metals Pb, Zn and Cd was much greater in the Hallen litter and soil system than within the Haw system (Table 2.3.1). Comparison of the profiles collected during the 1980's suggests that the Hallen burden was 1.77 times as great for Pb, 2.02 times as great for Cd, 1.64 times as great for Zn and 0.95 times as great for Cu (in relation to Haw). The percentage burden of metals in the litter was greater in the Haw soil / litter system than the Hallen soil / litter system. A large proportion of the Pb burden was held in the litter at both woodland sites. The overlying trend of heavy metal accumulation or loss within the Hallen and Haw soil / litter systems to 46cm depth will inevitably become more clearly established if further soil profiles are taken during the 1990's. There is already some suggestion that Pb is accumulating within the top 46cm of Hallen soil and litter, whereas Cd and Zn are being lost from the Hallen system (i.e. from 0 to 46cm soil depth). In comparison with soils that were relatively uncontaminated (e.g. Heinrichs and Mayer 1977, Van Hook *et al.* 1977) the Hallen and Haw Wood soil profiles have much greater heavy metal contamination within their mineral soil profiles:

## Table 2.3.1 Quantity of Heavy Metals ($mg/m^2$) in Haw Wood and Hallen Wood Soils to 46cm Depth

| | Total Metal in Soils ($mg/m^2$) + Litter | | % Metal Burden in Litter | |
|---|---|---|---|---|
| | | Lead | | |
| | Haw | Hallen | Haw | Hallen |
| 1975 | - | 27563 | - | 37.6 |
| 1979 | 28869 | 61823 | 38.8 | 49.5 |
| 1984-87 | 40598 | 72018 | 47.8 | 64.2 |
| | | Zinc | | |
| | Haw | Hallen | Haw | Hallen |
| 1975 | - | 143157 | - | 21.9 |
| 1979 | 93765 | 277148 | 16.2 | 9.8 |
| 1984-87 | 144079 | 235935 | 17.4 | 11.9 |
| | | Cadmium | | |
| | Haw | Hallen | Haw | Hallen |
| 1975 | - | 2331 | - | 34.4 |
| 1979 | 989 | 3890 | 29.7 | 13.7 |
| 1984-87 | 1574 | 3173 | 27.0 | 12.3 |
| | | Copper | | |
| | Haw | Hallen | Haw | Hallen |
| 1975 | - | 12443 | - | 5.9 |
| 1979 | 20719 | 13359 | 2.96 | 11.9 |
| 1984-87 | 16728 | 16125 | 8.10 | 14.1 |

Heavy Metal Burden in Mineral Soil ($mg/m^2$)

| | Claiborne Soil to 100cm depth (after Van Hook *et al* 1977) | Hallen Soil to 83.5cm depth |
|---|---|---|
| Cd | 90 | 3240 |
| Pb | 37000 | 48995 |
| Zn | 35800 | 277582 |

In comparison to the Claiborne Soil, the 1987 Hallen mineral soil profile has more than 36 times the amount of Cd, 8 times the amount of Zn and 1.3 times the amount of Pb. The data for heavy metals (mg/kg) in German beech and spruce forest soils are shown below:

Heavy Metal Burden ($mg/m^2$) in German Beech and Spruce Forest Soil (Heinrichs and Mayer 1977)

| Horizon Depth (cm)* | Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| 0-10 | 6.4 | 2800 | 7020 | 4400 |
| 10-20 | 7.1 | 2100 | 2500 | 6000 |
| 20-30 | 8.4 | 2600 | 2030 | 6600 |
| 30-40 | 9.6 | 3000 | 1560 | 7200 |
| 40-50 | 14.2 | 2500 | 1780 | 7300 |

* : data for 20-30cm = assumed average figure

The comparative data for Haw 1987 and Hallen 1987 profiles are displayed in Table 2.3.2. In general, the burden of Cd, Zn and Pb is greater in the Haw and Hallen 1987 soils than within the German forest soils. The concentrations of the German soil horizons range from 0.06-0.1 mg/kg for Cd, 17-24 mg/kg for Cu, 12-61 mg/kg for Pb and 38-55 mg/kg for Zn. These concentrations are typically background heavy metal concentrations for mineral soil when seen in context with the discussion in Section 2.2.2. Such values perhaps suggest the degree to which Cd, Cu, Pb and Zn have moved down the Haw and Hallen Wood mineral soil profiles in relation to relatively uncontaminated soil horizons.

Comparison of heavy metal levels in the top 25cm of Haw / Hallen Wood mineral soils with heavy metal levels in contaminated urban dune soil and wetland soil sites of north west Indiana, USA, is shown below:

## Table 2.3.2 Quantity of Heavy Metals (mg/m2) in Haw 1987 and Hallen 1987 Mineral Soil Profiles to 50cm Depth.

The "Factor" by Which the Burden of Heavy Metals in the Haw and Hallen Profiles Exceeds the Burden of Metals in the German Beech and Spruce Forest Soil Horizons is also Shown in Parentheses

Heavy Metal Burden in Haw 1987 Mineral Soil

| Horizon Depth (cm) | Quantity ($mg/m^2$) Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| 0-10 | 1116 (174) | 2980 (1.1) | 14334 (2.0) | 75622 (17) |
| 10-20 | 183 (26) | 2979 (1.4) | 5178 (2.1) | 23115 (3.9) |
| 20-30 | 116 (14) | 3397 (1.3) | 4543 (2.2) | 14595 (2.2) |
| 30-40 | 73 (7.6) | 3954 (1.3) | 3357 (2.2) | 10462 (1.5) |
| 40-50 | 40 (2.9) | 4135 (1.7) | 2896 (1.6) | 5936 (0.8) |

Heavy Metal Burden in Hallen 1987 Mineral Soil

| Horizon Depth (cm) | Quantity ($mg/m^2$) Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| 0-10 | 535 (84) | 2535 (0.9) | 18632 (2.7) | 36532 (8.3) |
| 10-20 | 655 (92) | 2411 (1.2) | 6677 (2.7) | 44356 (7.4) |
| 20-30 | 736 (91) | 2739 (1.1) | 4928 (2.4) | 52997 (8.0) |
| 30-40 | 653 (86) | 3281 (1.1) | 5155 (3.3) | 52820 (7.3) |
| 40-50 | 408 (29) | 3694 (1.5) | 5225 (2.9) | 41987 (5.8) |

Heavy Metal Burden ($mg/m^2$) in Mineral Soils to 25cm Depth

| | Indiana urban soils Parker *et al* (1978) | | Woodland soils in the vicinity of Avonmouth | |
|---|---|---|---|---|
| | Dune | Wetland | Haw 1987 | Hallen 1987 |
| Cd | 476 | 446 | 1366 | 1575 |
| Cu | 4500 | 5500 | 7564 | 6291 |
| Pb | 18300 | 18400 | 21646 | 27964 |
| Zn | 107100 | 123100 | 106549 | 107519 |

Essentially, the heavy metal burden in the top 25cm of Haw and Hallen soils exceeds that of the dune and wetland soils by 2.9-3.5 times for Cd, 1.1-1.7 times for Cu, 1.2-1.5 times for Pb and 0.9-1.0 times for Zn. Parker *et al.* (1978) considered that their Indiana urban sites were heavily contaminated with Cd, Zn, Pb and Cu, and that the soil was a major reservoir in retaining such metals. The Avonmouth woodland Cu, Pb and Zn metal burden data are not too dissimilar to the relative Indiana values, whereas the Cd burden values within the Avonmouth soils are at least 3 times larger than the Indiana Cd data.

The degree to which the Indiana urban soils and the Avonmouth woodland soils have been contaminated by Cu and Pb would appear to be relatively minimal when compared to the Cu and Pb metal burdens recorded for uncontaminated sites by Van Hook *et al.* (1977) and Heinrichs and Mayer (1977). With respect to the relatively uncontaminated Claiborne soil, the contaminated Hallen 1987 soil contained only 1.3 times as much Pb. If an estimated additional Pb burden is added to the Hallen soil Pb content to take the metal burden to an equivalent 1 metre soil depth (assuming that the soil bulk density and Pb soil concentration was the same as the data recorded at the base of the Hallen profile), then the revised total Pb burden at 52560 $mg/m^2$ would only be 1.4 times greater than the Claiborne Pb burden. Likewise, in comparison to the Cu burden within the German beech and spruce forest soils, the Haw Cu burden to 50cm depth was only 1.3 times as great. As the highest burdens of Pb and Cu were found in the Hallen 1987 and Haw 1987 profiles respectively, it would appear that contamination of Indiana urban, Haw 1987 and Hallen 1987 soils by these two metals was not overly excessive in comparison to the uncontaminated sites. But it should be pointed out that consideration of soil profiles to great depth could effectively dilute / mask any surface contamination of a metal such as Pb. However, the Cd and Zn burdens in the former polluted soils (with respect to the latter uncontaminated soils) were

much greater. The Cd burden, particularly, was much greater at the contaminated sites. This, perhaps, has been somewhat exaggerated by the low background concentrations that occurred for Cd within the uncontaminated soils.

The higher degree by which Haw and Hallen mineral soils have been contaminated by Cd and Zn is suggested by comparison of the Haw/Hallen Cd and Zn metal burdens with those of the relatively uncontaminated forest soil sites reported by Van Hook *et al.*(1977) and Heinrichs and Mayer (1977). The degree of heavy metal movement down the Haw and Hallen soil profiles has been much more extensive at the Hallen site; metal movement being more lucidly expressed by Cd and Zn to deeper soil horizons, whereas Pb and Cu movement is not clearly expressed and is superficial and / or minimal within the mineral soil.

## 2.3.4. Cadmium and Zinc Movement down Hallen Wood Soil Profiles

The redistribution of Zn and Cd down the Hallen soil profiles with time, as illustrated in Figs.2.3.8 and 2.3.10 respectively, has principally been attributed to progressive acidification to pH values below 6 to substantial soil depths (Martin and Coughtrey 1987). Martin and Coughtrey (1987) considered that the evidence from nearby woodlands on similar soil parent material to that of the Hallen site (but less heavily contaminated) suggested that the soil pH of the Hallen Wood soil would have been near neutral in the surface mineral layers when smelting first began at Avonmouth in 1928.

pH data (soil : water ratio 1:2.5) collected by the Soil Survey for soil profiles which represent the Denchworth, Worcester and other related soil series in Gloucestershire, Somerset, Avon and North Wiltshire suggest that most of these silty-clay soils maintain pH regimes that are circa neutral (pH6.0-pH8.0). The ranges of pH recorded in A, B and C horizons of these soils have been collected from Findlay (1965, 1976), Cope (1973) and Colborne (1981) and are shown below:

| Soil Series | pH Range | No. of Profiles |
|---|---|---|
| Denchworth | 5.3-8.4 | 5 |
| Worcester | 6.2-8.7 | 8 |
| Evesham | 6.2-8.5 | 12 |
| Hurcot | 5.8-8.2 | 2 |
| Spetchley | 5.4-8.5 | 4 |
| Whimple | 6.2-8.0 | 4 |

| | | |
|---|---|---|
| Wedmore | 5.6-7.6 | 2 |
| Greinton | 6.0-7.9 | 3 |
| Holwell | 6.0-8.1 | 2 |

The most acidic profile recorded by the Soil Survey was a Denchworth Series soil profile at Manor Farm, Grittleton, Wiltshire, 32km west of the Avonmouth smelter (Findlay 1976). The pH data recorded for this profile have been used in Fig.2.3.12 where the available pH data for Haw and Hallen woodland soils have been plotted. The pH data for the Wetmoor woodland topsoil (located 23km ENE of the Avonmouth smelter) has also been included as the soil parent material was Lower Lias clay. Geographically, in relation to Hallen and Haw Wood, Wetmoor is located at the opposite (northern) end of the Tortworth Ridge within the Vale of Sodbury. Haw soil pH's conform to pH's recorded at Wetmoor and by the Soil Survey. However, the Hallen soil pH's are clearly much more acidic (even at depth). Since 1973, when Hallen topsoil pH's were at about pH5 and above, the pH's have latterly been recorded as less than pH5 in the topsoil. Furthermore, apart from the 1987 pH data, the Hallen topsoil pH has been recorded at pH4.0 or less during the 1980's. Such low pH recordings are not characteristic of soils (such as those found at Haw and Hallen Wood) which would be expected to have a reasonably high percentage base status. Fig.2.3.13 demonstrates that Hallen 1987 soil had a low base status particularly in the surface soil where pH's were <pH5. The % base saturation in the surface soil at Haw Wood was much higher.

The strongly acidic soil reaction that has been determined in Hallen soil, combined with the low base status of the soil, does not ideally conform to the ecological requirements of the Pedunculate oak, *Quercus robur*, which grows in Hallen Wood. Gardiner (1974) suggested that, as regards habitat requirements, there was a tendency displayed by *Quercus robur* for basic soils rich in nutrients, which was linked to a preference for moist clays combined with a tolerance of waterlogging and even flooding. Little (1974) measured soil reaction of *c.* pH6 in the early 1970's at Hallen Wood. The disappearance of a species such as *Mercurialis perennis* from the ground flora of Hallen Wood since the 1970's suggests that the soil pH's used to be higher than have been measured latterly.

The strongly acidic soil reactions within the Hallen soil would encourage more mobile heavy metals such as Cd and Zn to move down the soil profile with time. There is a growing recognition that soil pH's between pH5-pH6 are important with respect to the adsorption / desorption reactions and mobility of Cd and Zn (e.g. Cavallaro and McBride 1984, Cottenie 1980, Jones and Jarvis 1981, Kabata-Pendias and Pendias 1984, Martin and Coughtrey 1987, Scokart

*et al.* 1983). Within the Hallen profile, soil pH has remained below pH5.5 within the topsoil since pH readings were first taken in 1973. Only since the 1980's have pH's been measured at pH5.5 and greater, but much deeper down the soil profile: pH's did not exceed pH5.5 in 1984 until 38.5cm depth, in 1985 until 48.5cm depth and in 1987 until 51-53.5cm depth. In addition, soils in the pH range pH5-pH6 have been suggested as having a low degree of pH buffering capacity (Magdoff and Bartlett 1985). Hence, any acidification of soil in the pH5-pH6 range may be more easily achieved than at other soil pH's.

Scokart *et al.* (1983) have suggested that the mobility of Cd and Zn in Belgian soils was not only associated with soil pH's that were below pH5-pH6, but also with the migration of organic matter down the soil profiles. Others have reported that soluble metal-organic complexes have been involved with metal movement down soil profiles (Lund *et al.* 1976, Stevenson and Welch 1979). Fig.2.3.14 illustrates the % carbon within the mineral soil profiles (1984-87) at Haw and Hallen Wood. The Haw profiles suggest that % carbon decreased with soil depth. The 1984 and 1987 Hallen profiles, however, suggest that some accumulation / translocation of organic matter might have occurred to depth. However, the percentage organic matter at depth in the Hallen and Haw profiles was moderately low and the Hallen 1985 percentage carbon profile suggests that translocation of organic matter down the Hallen soil was not necessarily associated with heavy metal movement. The higher levels of organic matter combined with the higher soil pH's in the Haw surface soil (in relation to the Hallen soil) should aid in the immobilization of heavy metals in the Haw topsoil.

## 2.4 . Summary and Conclusions

a) The behaviour of heavy metals within a soil will depend upon the biological, chemical and physical nature of the soil in relation to the environmental factors which affect it. Adsorption processes (non-specific adsorption, specific adsorption, organic complexation and co-precipitation) play an important part in affecting the behaviour and bioavailability of heavy metals in soils. The most important soil constituents which contribute to and compete for the sorption of heavy metals are clay minerals, hydrated metal oxides/oxides and organic matter. Pb and Cu demonstrate a greater affinity for adsorption upon these constituents in relation to Cd and Zn, such that the relative retention and selective adsorption of heavy metals by soils follows the order:

Pb, Cu > Zn, Cd

Environmental factors such as pH and pE play an important role in modifying / influencing the adsorption capacities of soils: the adsorption capacity of a soil being an important component with respect to the soil's ability to retain and immobilize heavy metals.

b) Forest soil / litter systems act as important heavy metal sinks. Atmospheric deposition of heavy metals can lead to high surficial concentrations of metals, especially in the organic litter layers. High concentrations of heavy metals can introduce stressful conditions for decomposition processes to occur, and accumulation of organic matter in woodland / forest floors can result. Input of contaminants within the soil / litter system leads to enhanced concentrations of heavy metals in forest floors / soils above what might be considered background metal concentrations.

c) Heavy metals have been viewed as having the ability to move down soil profiles. The circumstances under which heavy metal mobility is more likely to be evident are where soils are acidic and sandy in nature. Cd and Zn are considered to be potentially more mobile than Cu and Pb under such conditions.

d) Results from soil profiles taken over time from two woodlands aerially contaminated with heavy metals suggest that both Hallen and Haw woodlands are heavily polluted in the surficial soil / litter layers. The highest metal concentrations occurred in the surface organic litter layers. Distinct concentration gradients have been maintained or enhanced for heavy metals in Haw Wood and for Cu and Pb in Hallen Wood. However, in Hallen Wood, Cd and Zn appear to have decreased in concentration with time in the organic litter layers and movement / redistribution of these metals can be discerned down the soil profiles with time. This has led to contamination of Hallen soil by Cd and Zn to depths approaching half a metre or more depending upon what is considered to be the background concentration of the soil. No conclusive signs of Pb and Cu movement were evident: a high proportion of the Pb burden being retained within the organic litter component.

e) One of the principal features of the soil at the Hallen site which would encourage the movement of Cd and Zn down the soil profiles is the strongly acidic reaction that has been recorded at the site since 1979.

The next Chapter attempts to identify / characterise the chemical speciation of the more mobile phases of heavy metals within the 1987 Haw and Hallen soil profiles.

Fig.2.3.1-2.3.4 Total Heavy Metal Concentrations in Hallen and Haw Wood Soil Profiles (a=Haw Wood profiles, b=Hallen Wood profiles).

Fig.2.3.1.=Zn
Fig.2.3.2.=Pb
Fig.2.3.3.=Cd
Fig.2.3.4.=Cu

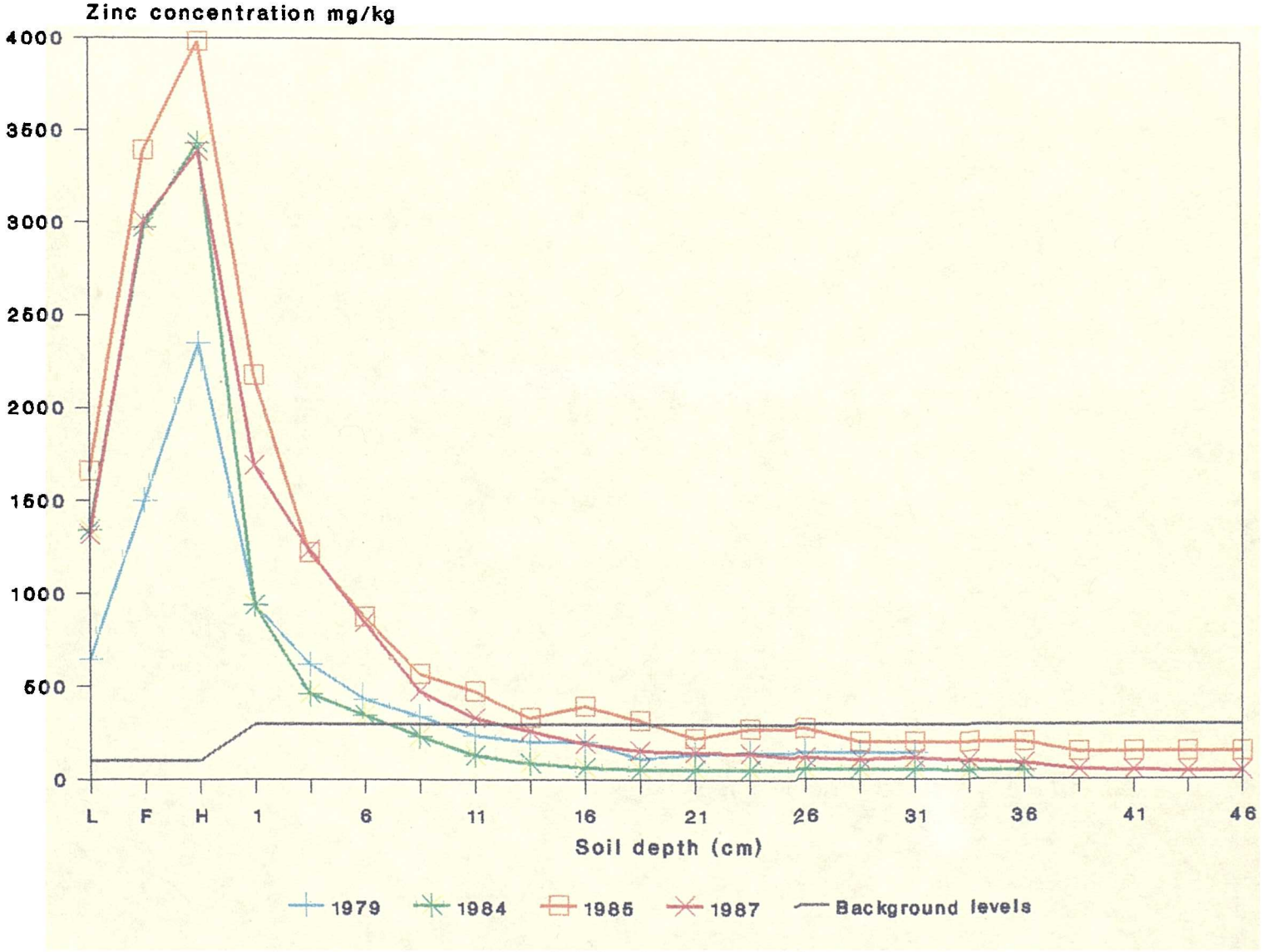


Fig.2.3.1a Haw Wood Zinc

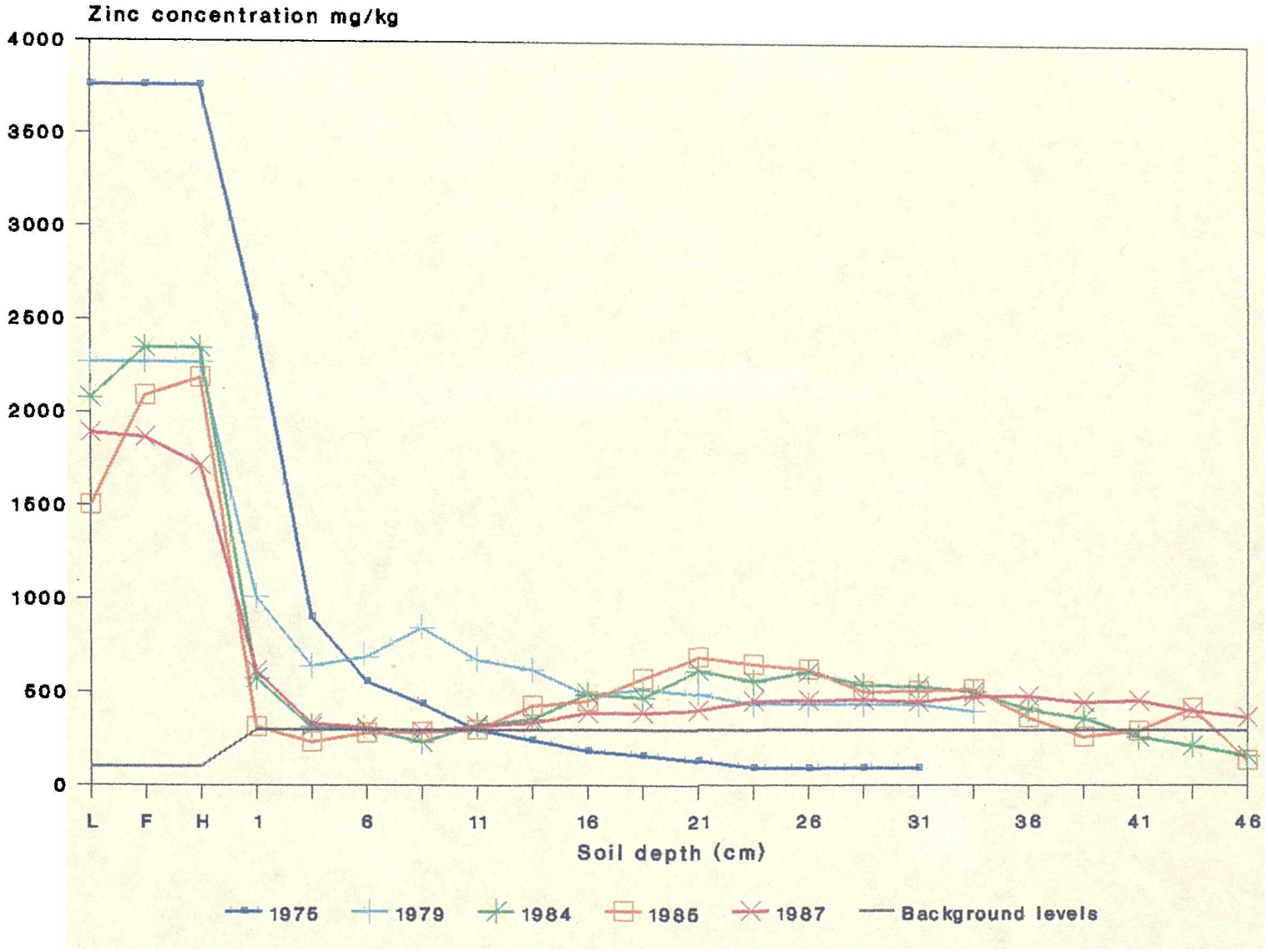


Fig.2.3.1b Hallen Wood Zinc

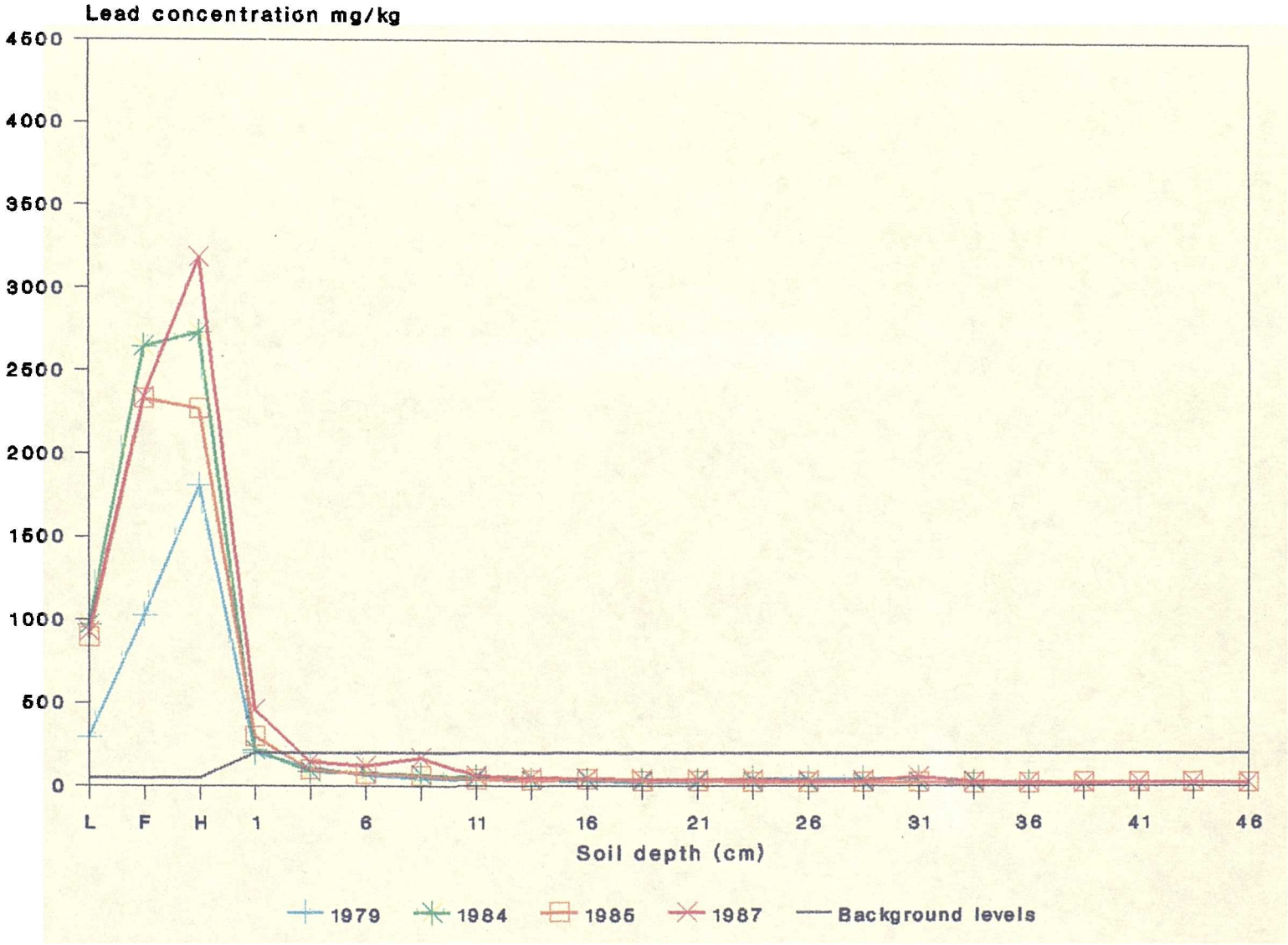


Fig.2.3.2a Haw Wood Lead

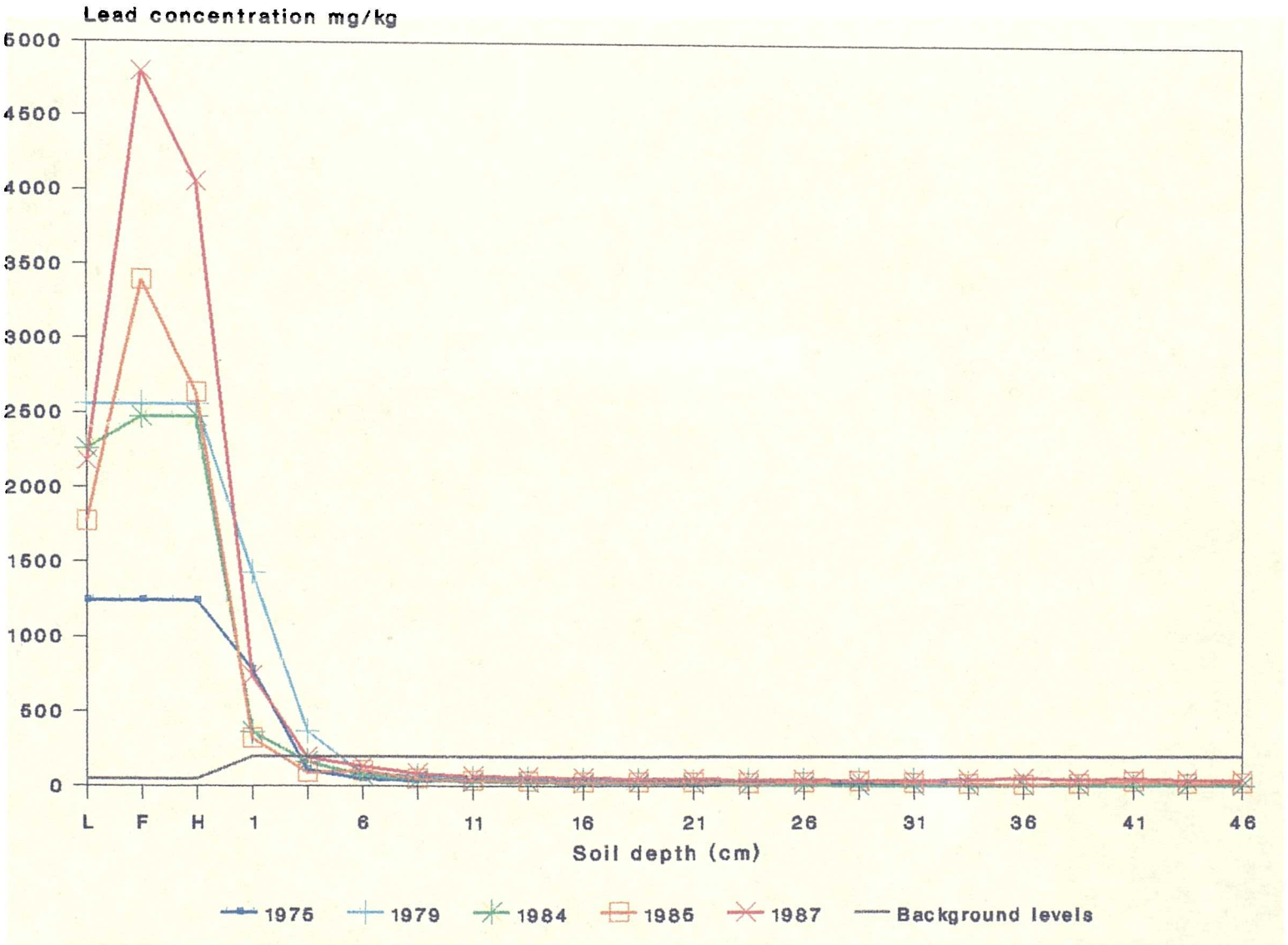


**Fig.2.3.2b Hallen Wood Lead**

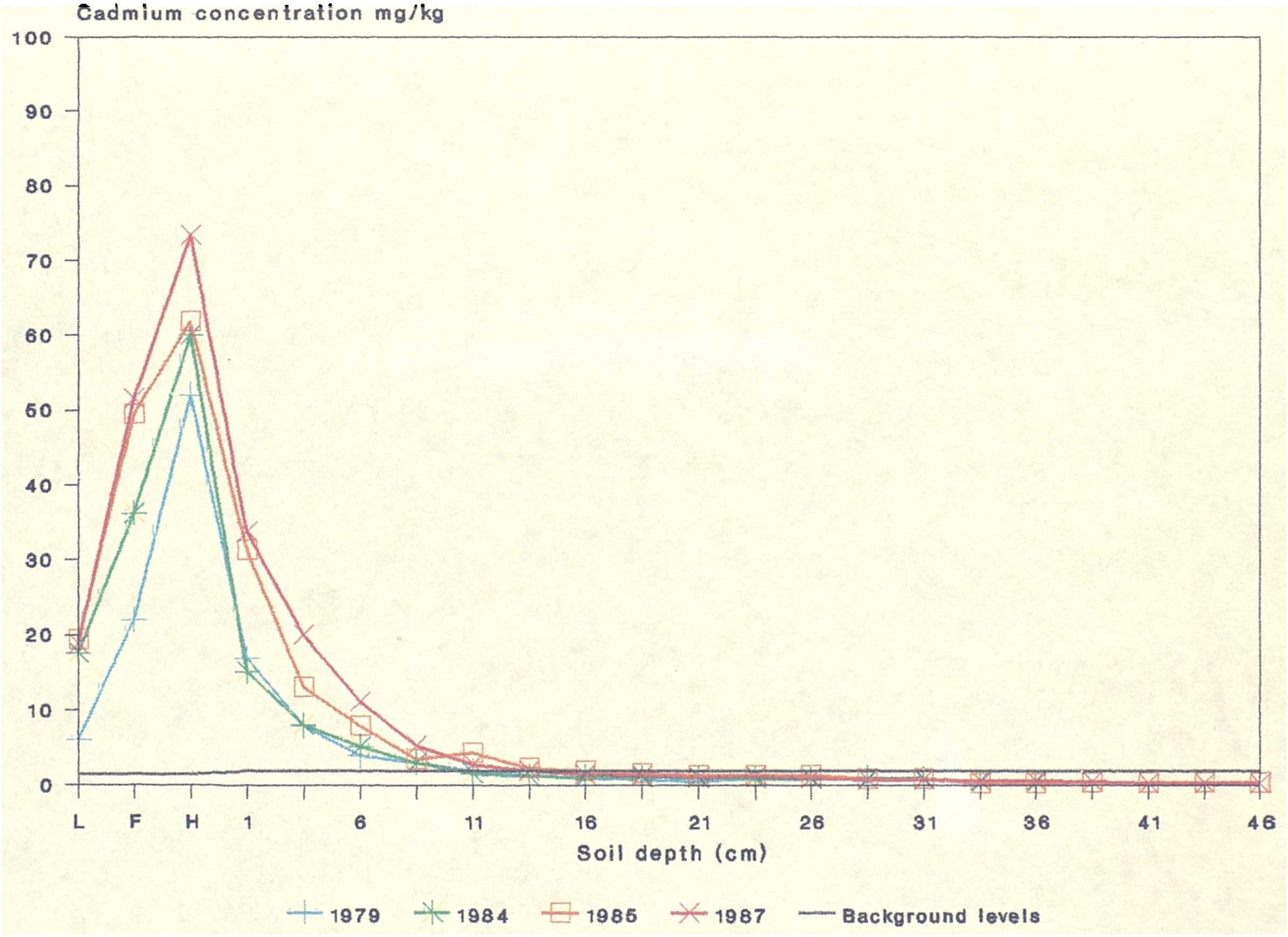


**Fig.2.3.3a Haw Wood Cadmium**

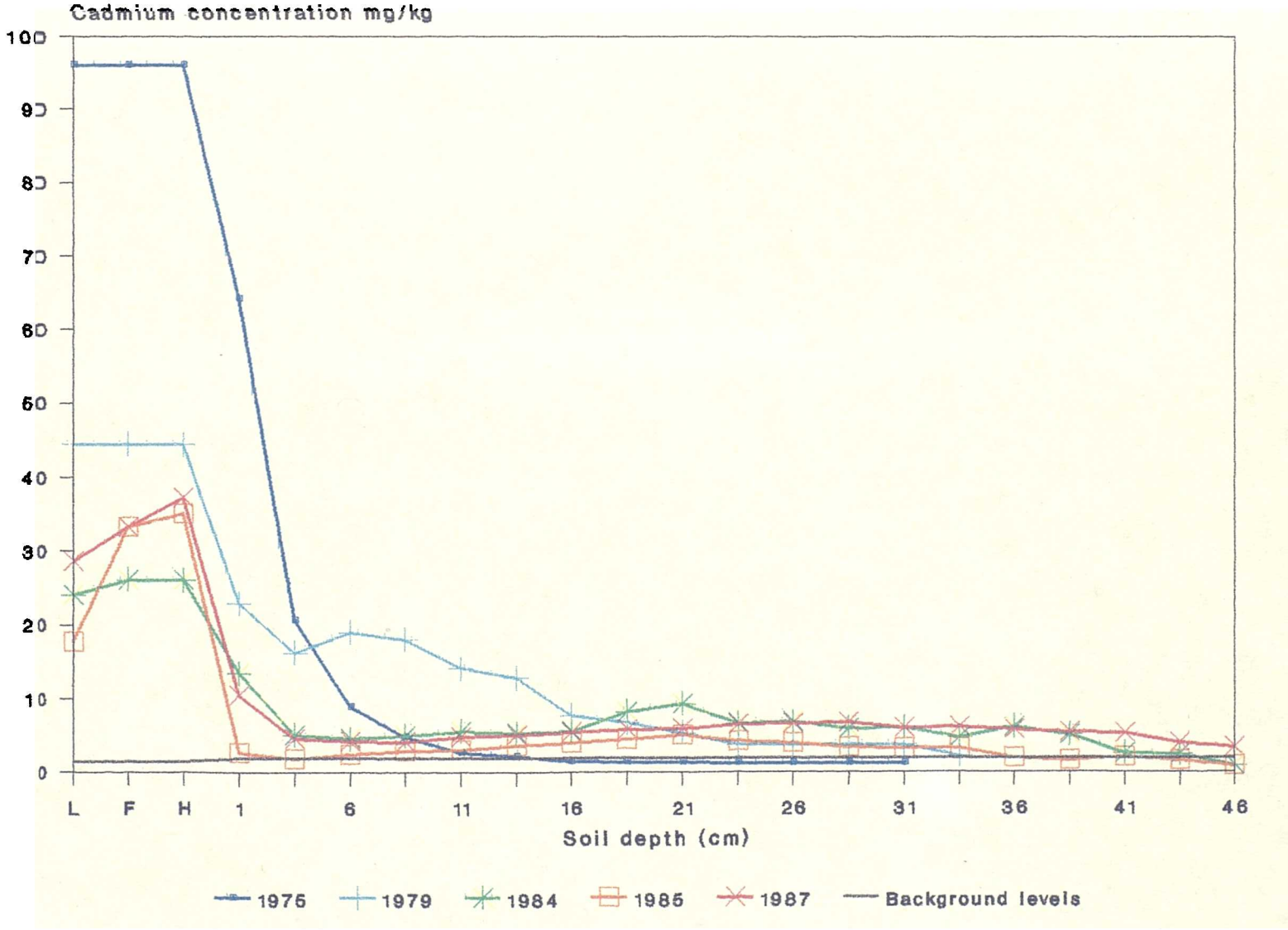


**Fig.2.3.3b Hallen Wood Cadmium**

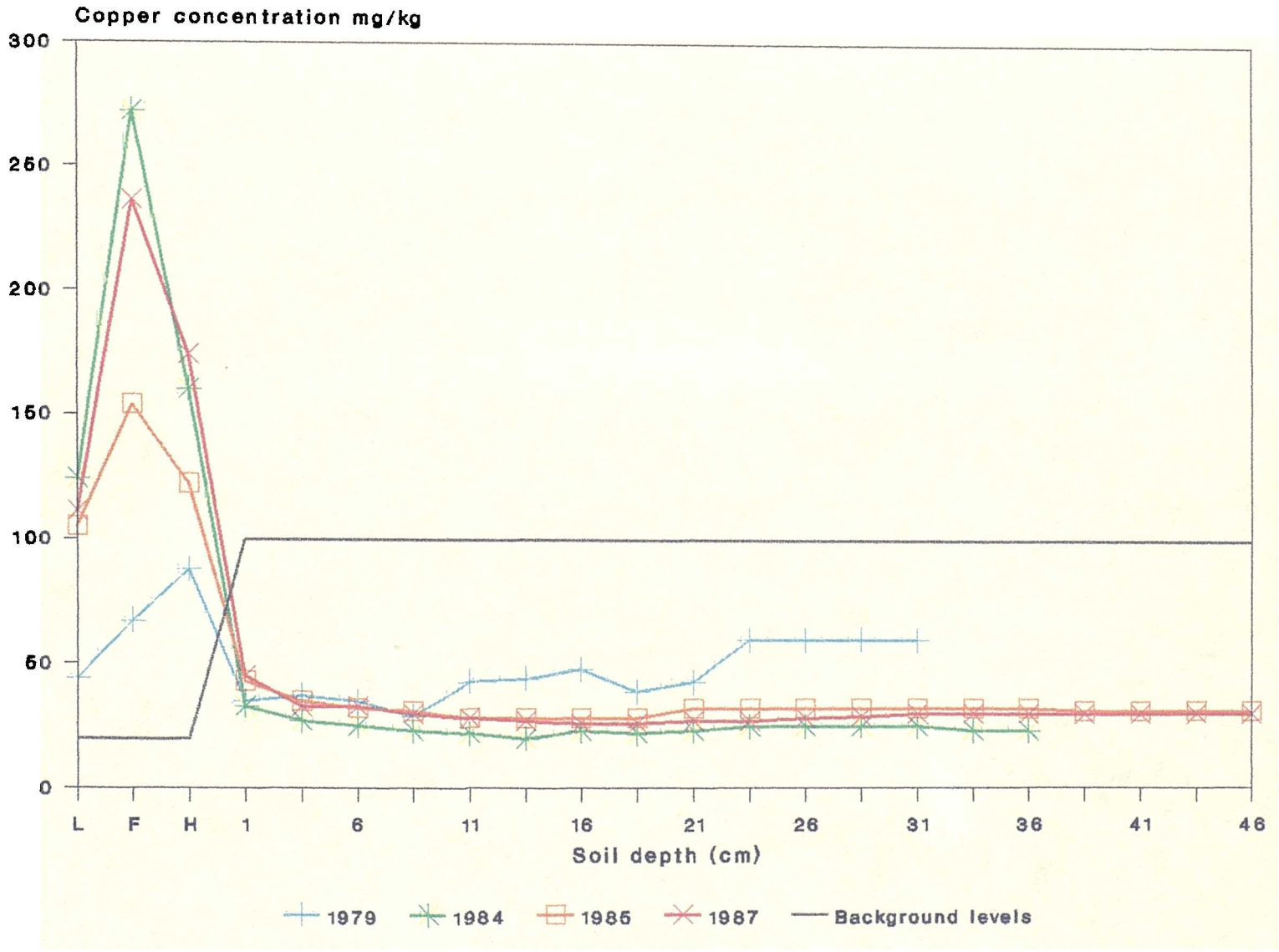


Fig.2.3.4a Haw Wood Copper

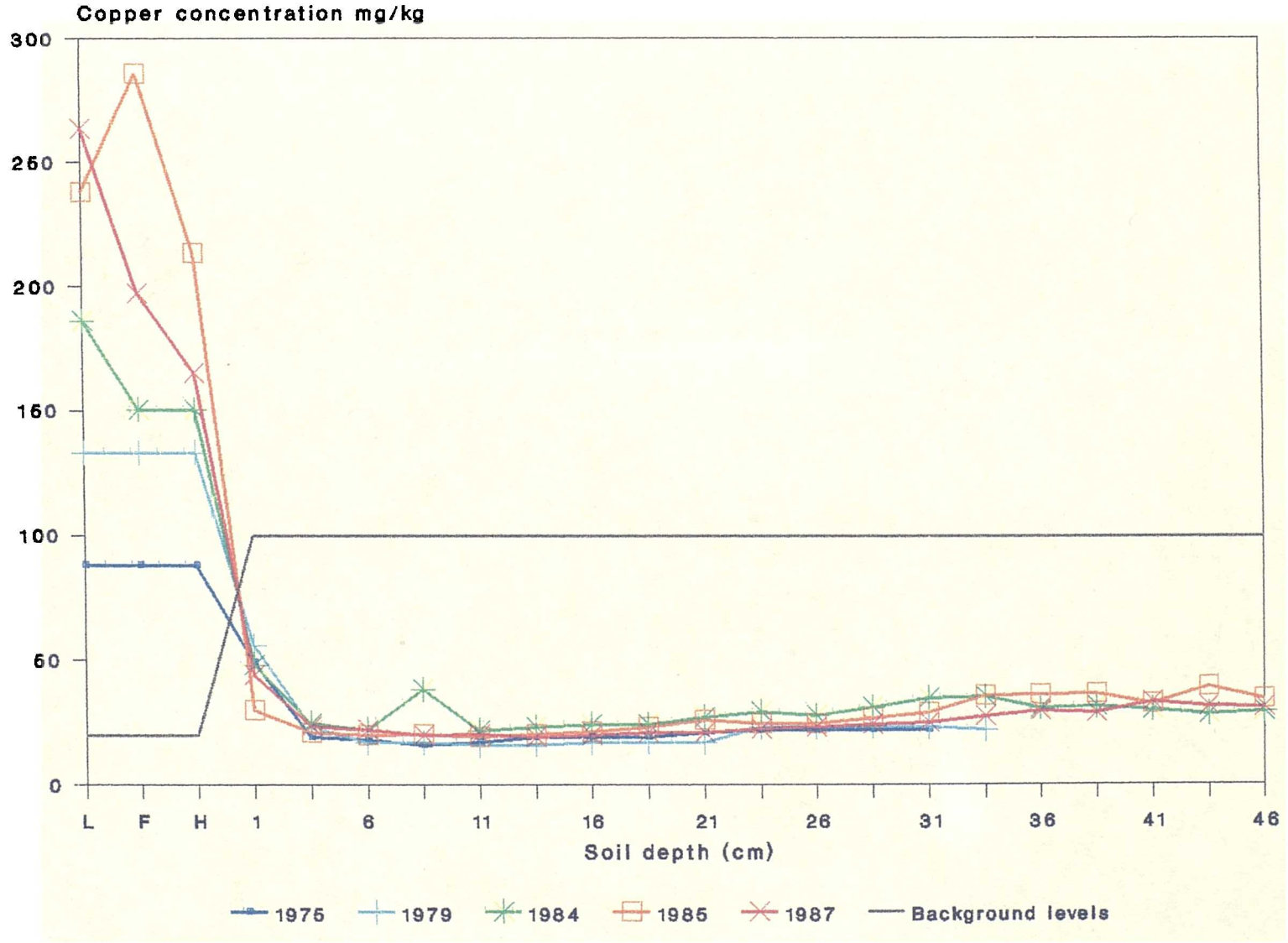


Fig.2.3.4b Hallen Wood Copper

Fig.2.3.5. 1987 Haw and Hallen Total Heavy Metal Concentrations in Mineral Soil Profiles.

(a)=Zn, (b)=Pb, (c)=Cd, (d)=Cu

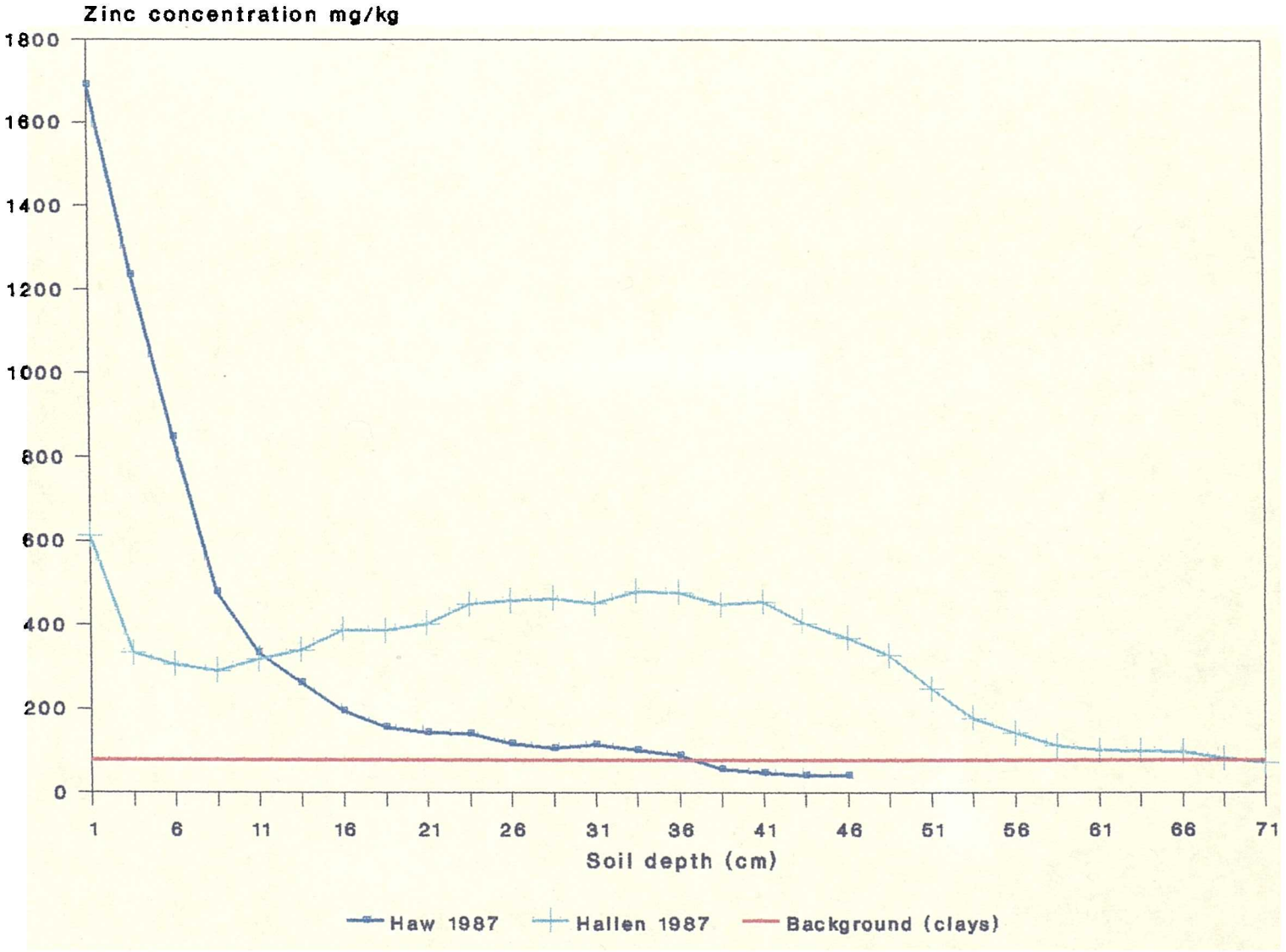


**Fig.2.3.5a 1987 Haw/Hallen Zinc**

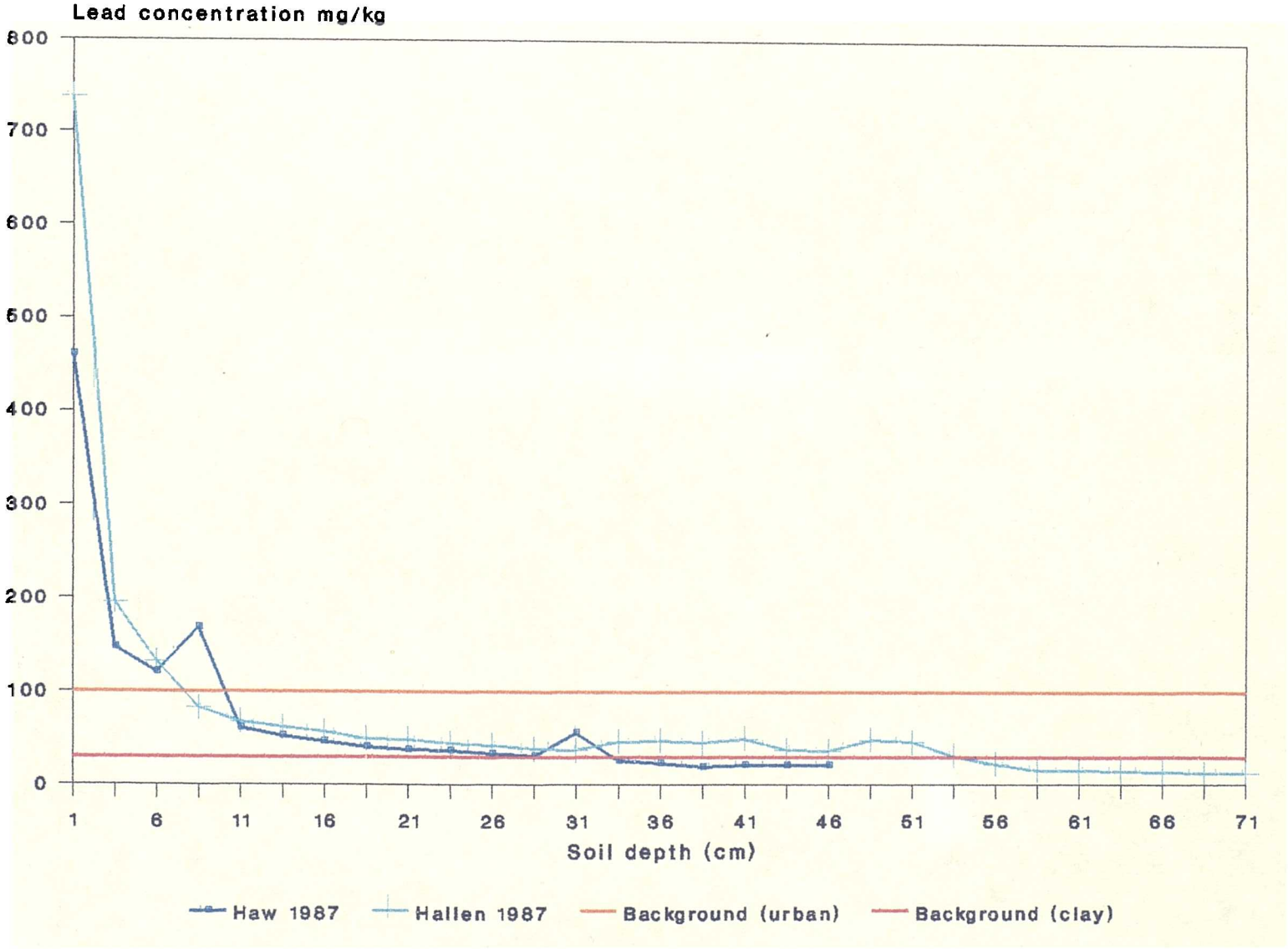


Fig.2.3.5b 1987 Haw/Hallen Lead

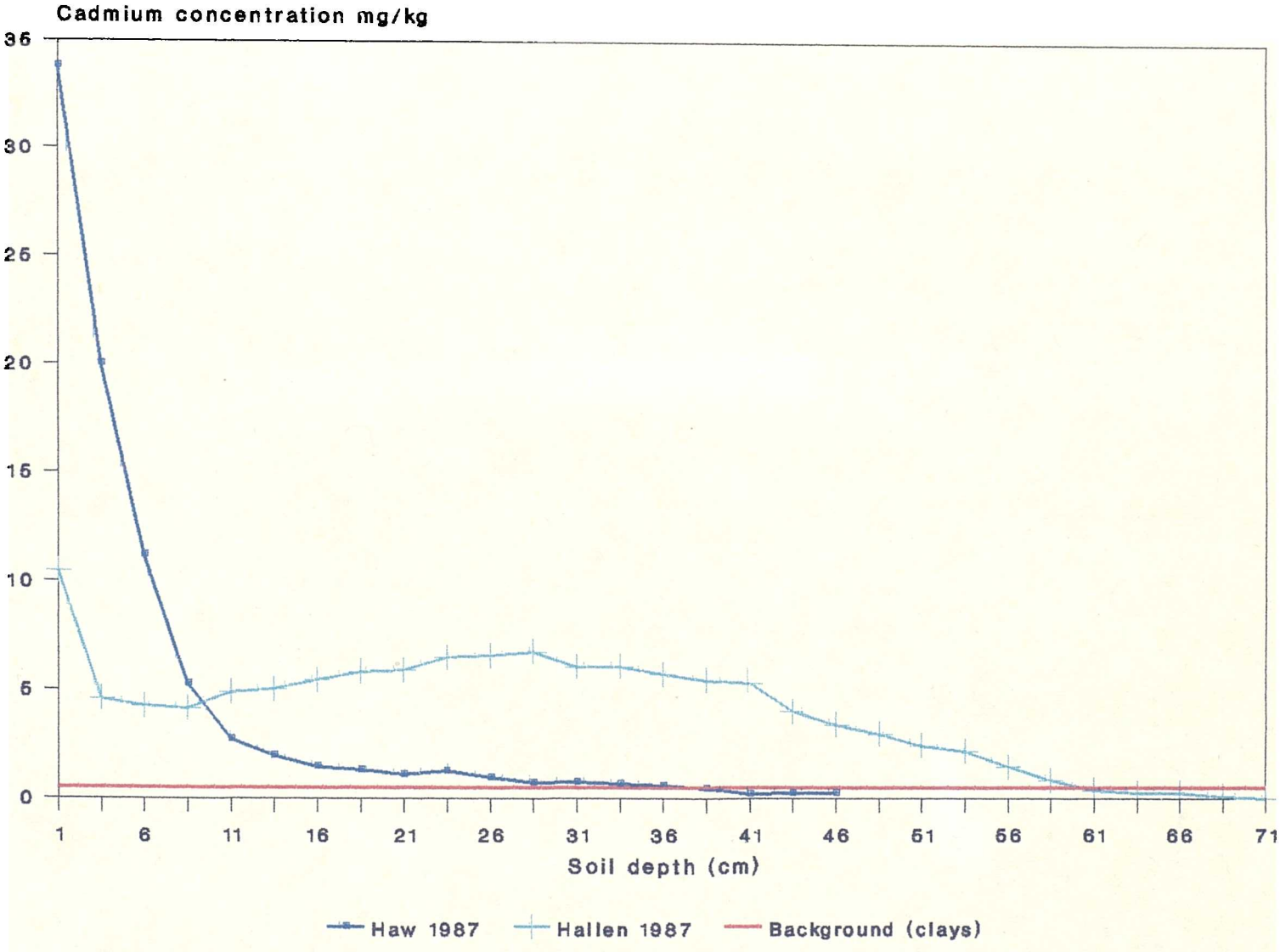


Fig.2.3.5c 1987 Haw/Hallen Cadmium

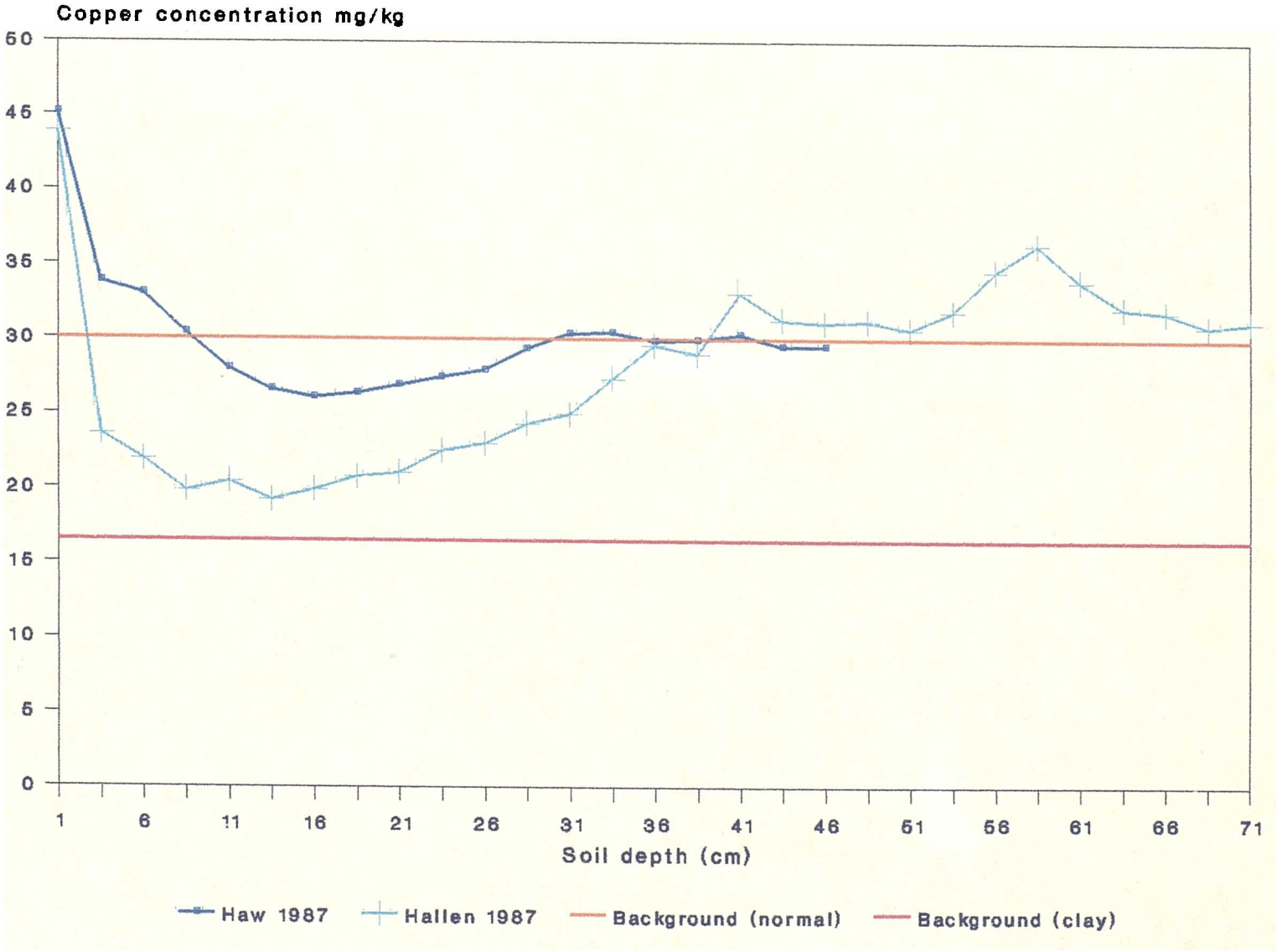


Fig.2.3.5d 1987 Haw/Hallen Copper

Fig.2.3.6. 1987 Hallen Core Profiles of Total Concentrations of Heavy Metals in the Soil Profile.

(a)=Zn, (b)=Pb, (c)=Cd, (d)=Cu

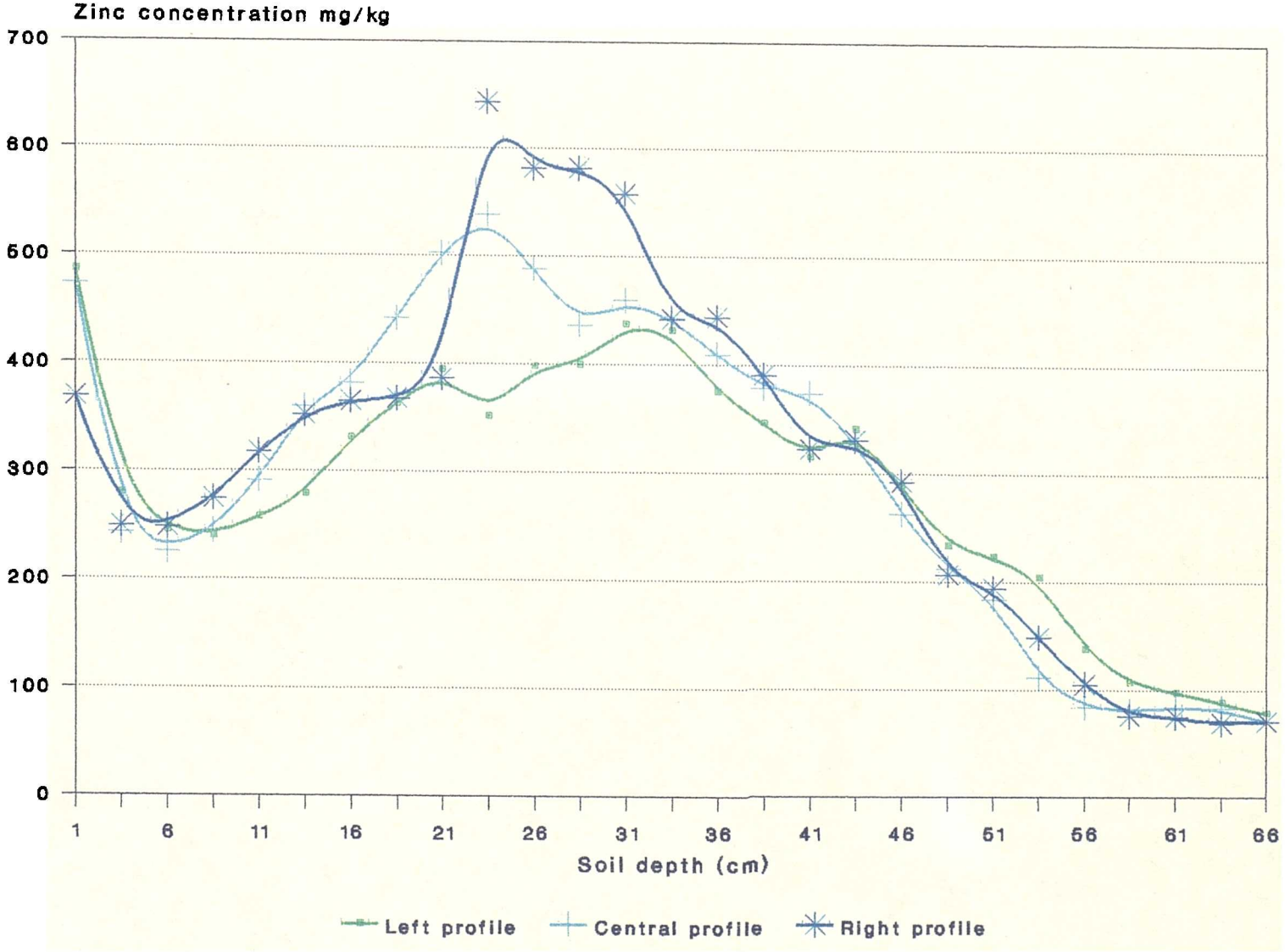


Fig.2.3.6a Core profiles: Zinc

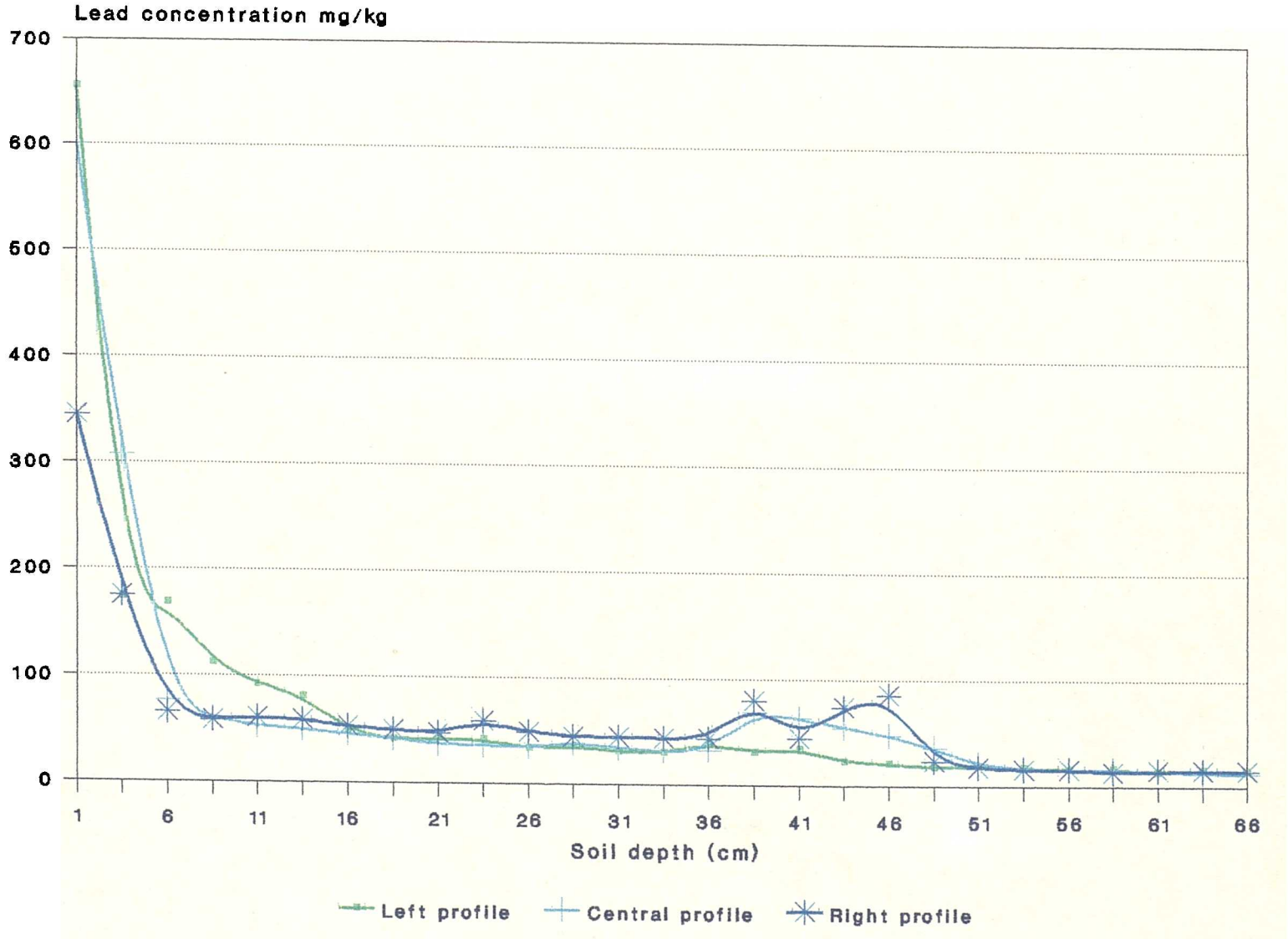


Fig.2.3.6b Core profiles: Lead


**Fig.2.3.6c Core Profiles: Cadmium**

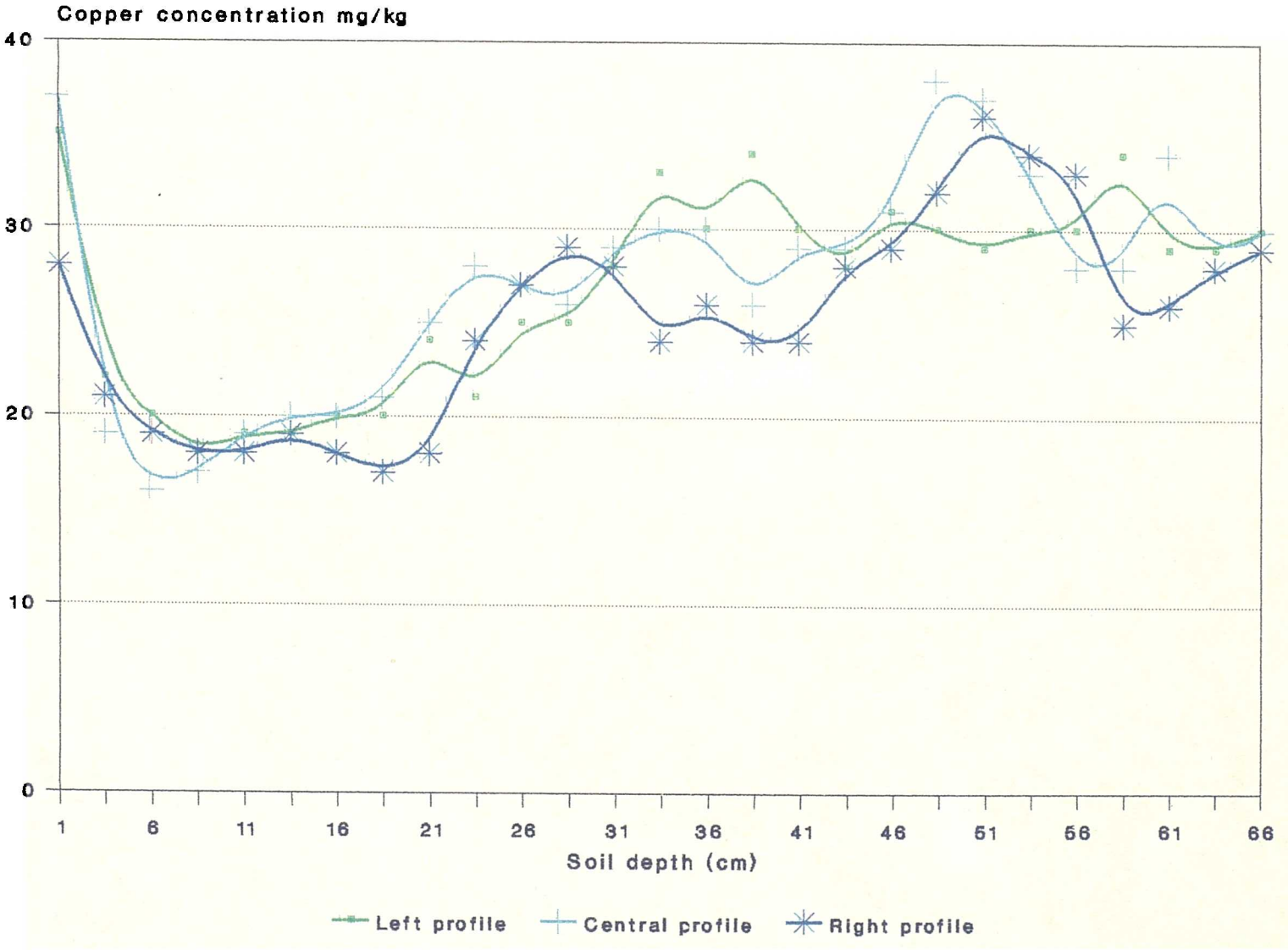


Fig.2.3.6d Core Profiles: Copper

Fig.2.3.7. Changes in the Distribution of Total Cd, Pb and Zn Concentrations with Time in the Hallen Wood Profile.

(a)=Cd, (b)=Zn, (c)=Pb

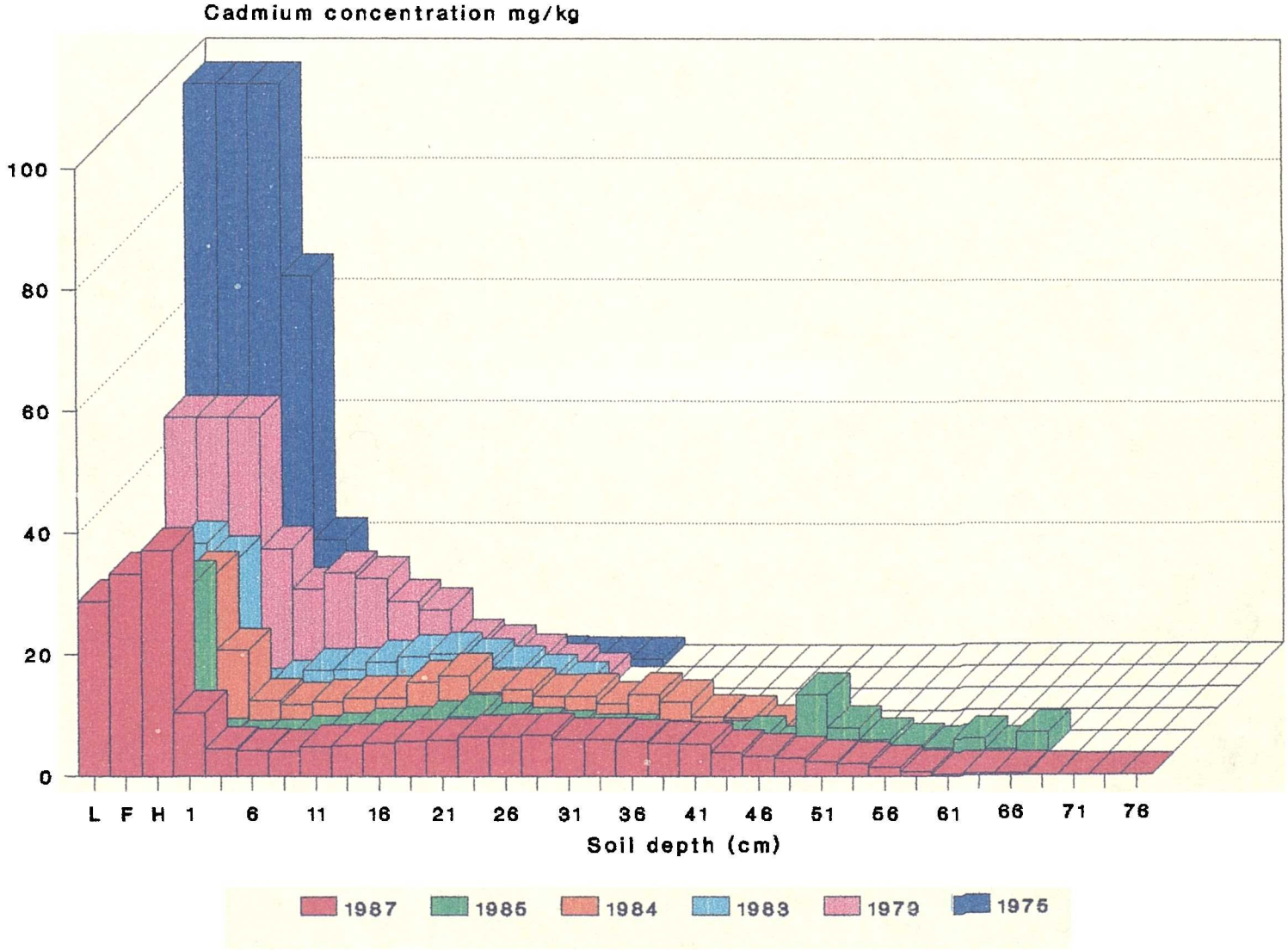


Fig.2.3.7a Cadmium concentrations in Hallen mineral soil profiles 1975-1987

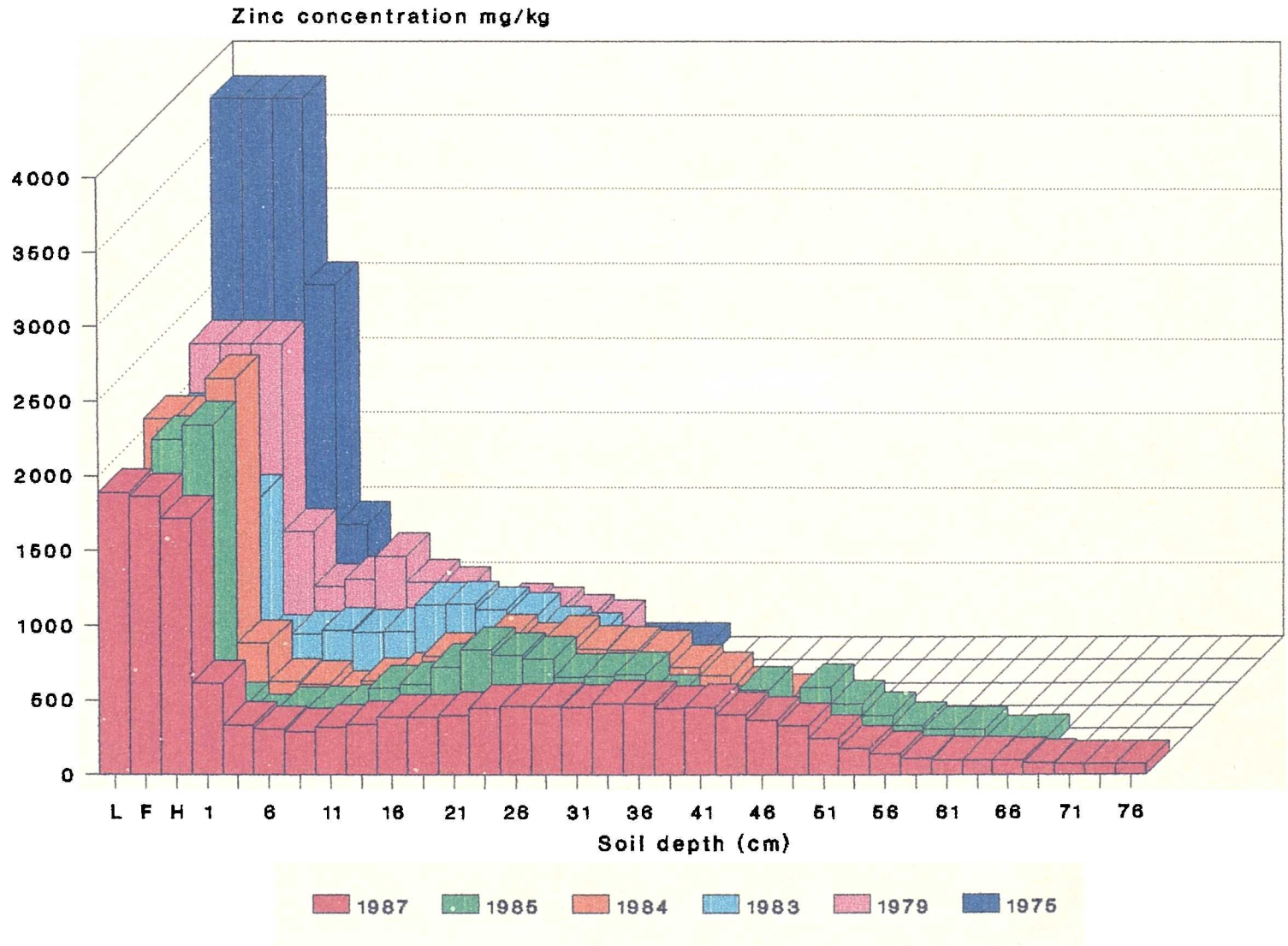


Fig.2.3.7b Zinc concentrations in the Hallen mineral soil profiles 1975-1987

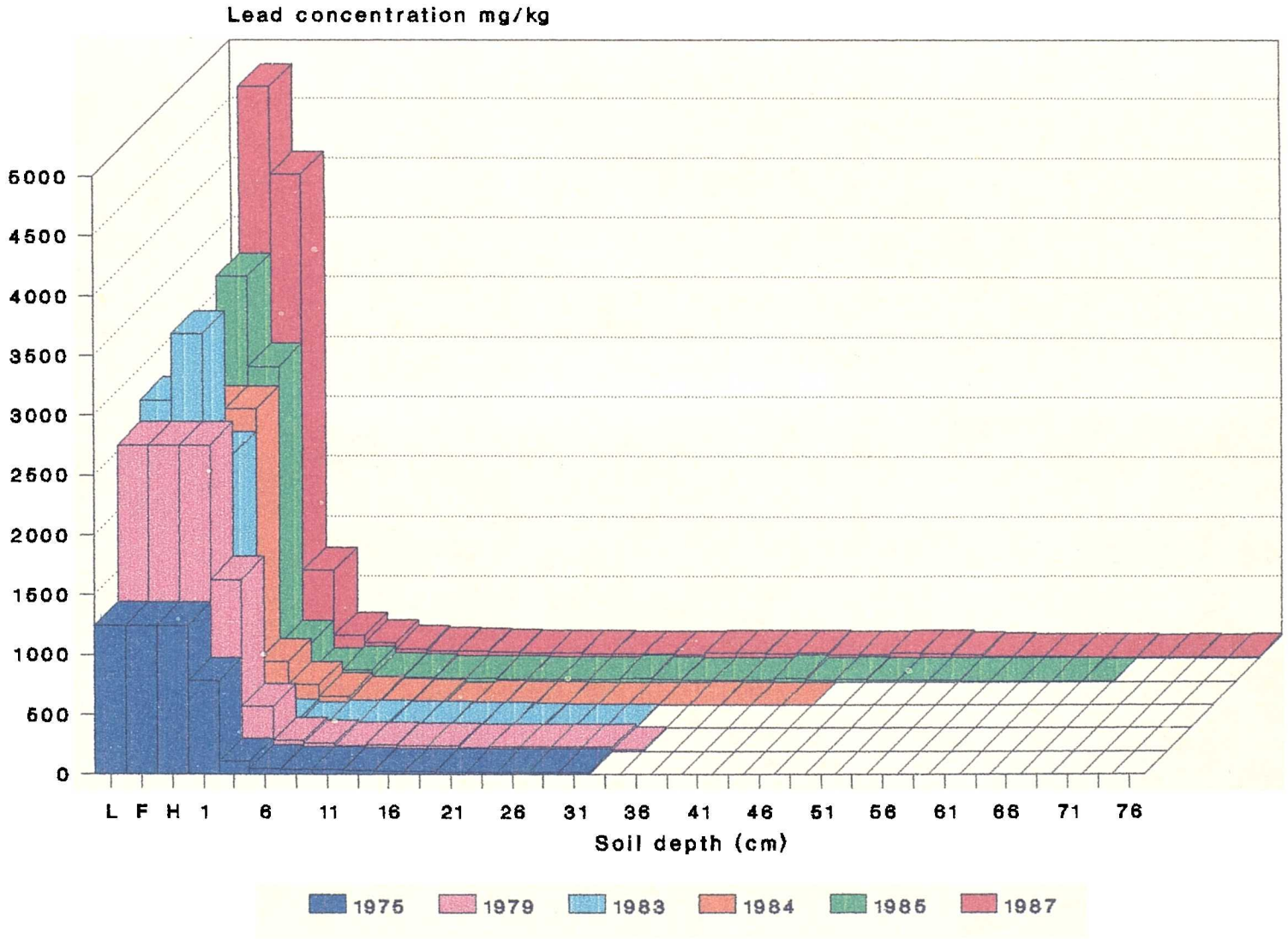


Fig.2.3.7c Lead concentrations in the Hallen mineral soil profiles 1975-1987

Fig.2.3.8-2.3.11. The Proportion of Heavy Metals in Each Soil Layer in Haw and Hallen Wood Soils (a=Haw, b=Hallen).

Fig.2.3.8.=Zn
Fig.2.3.9.=Pb
Fig.2.3.10.=Cd
Fig.2.3.11.=Cu

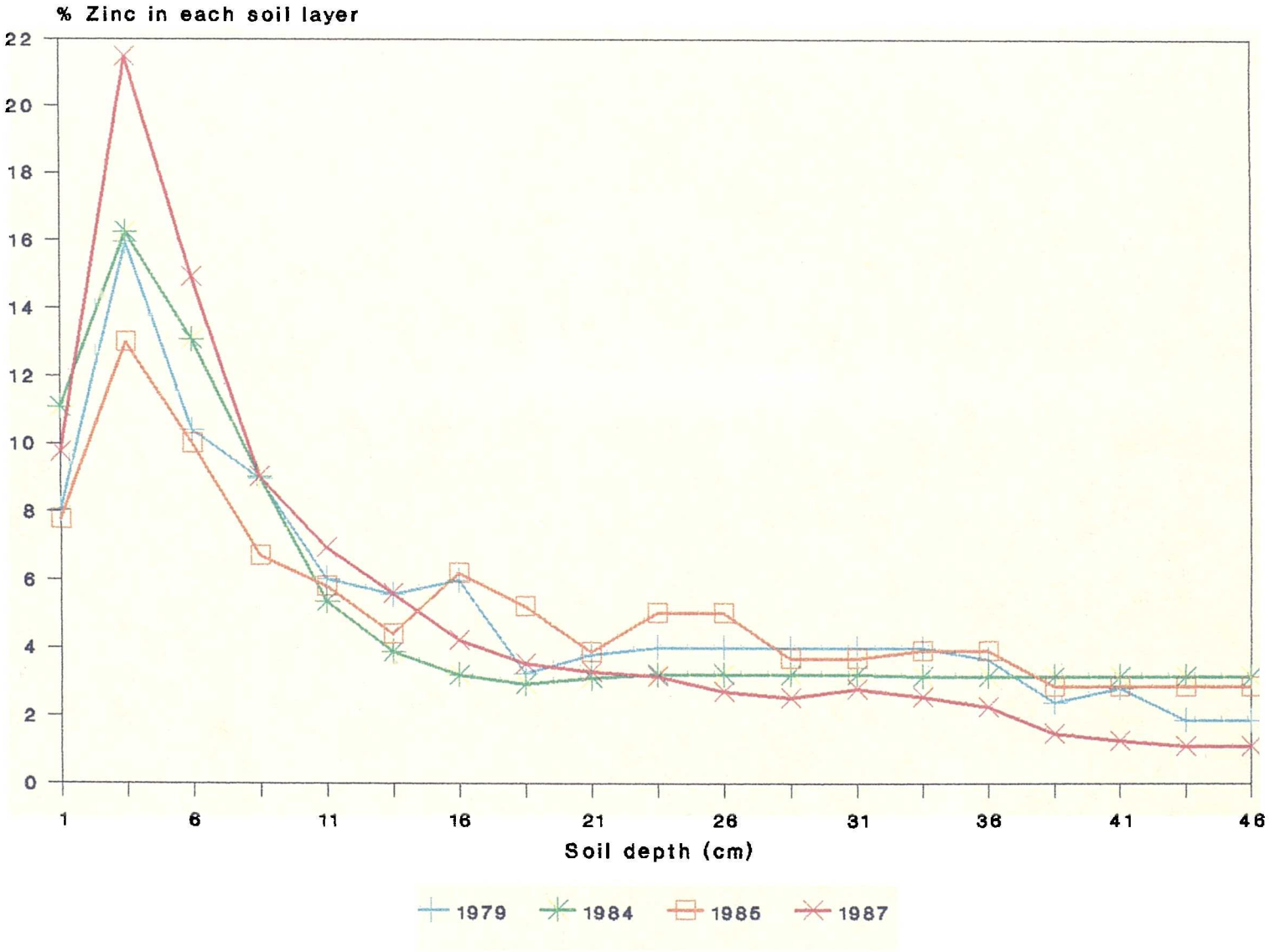


Fig.2.3.8a Haw Wood Zinc

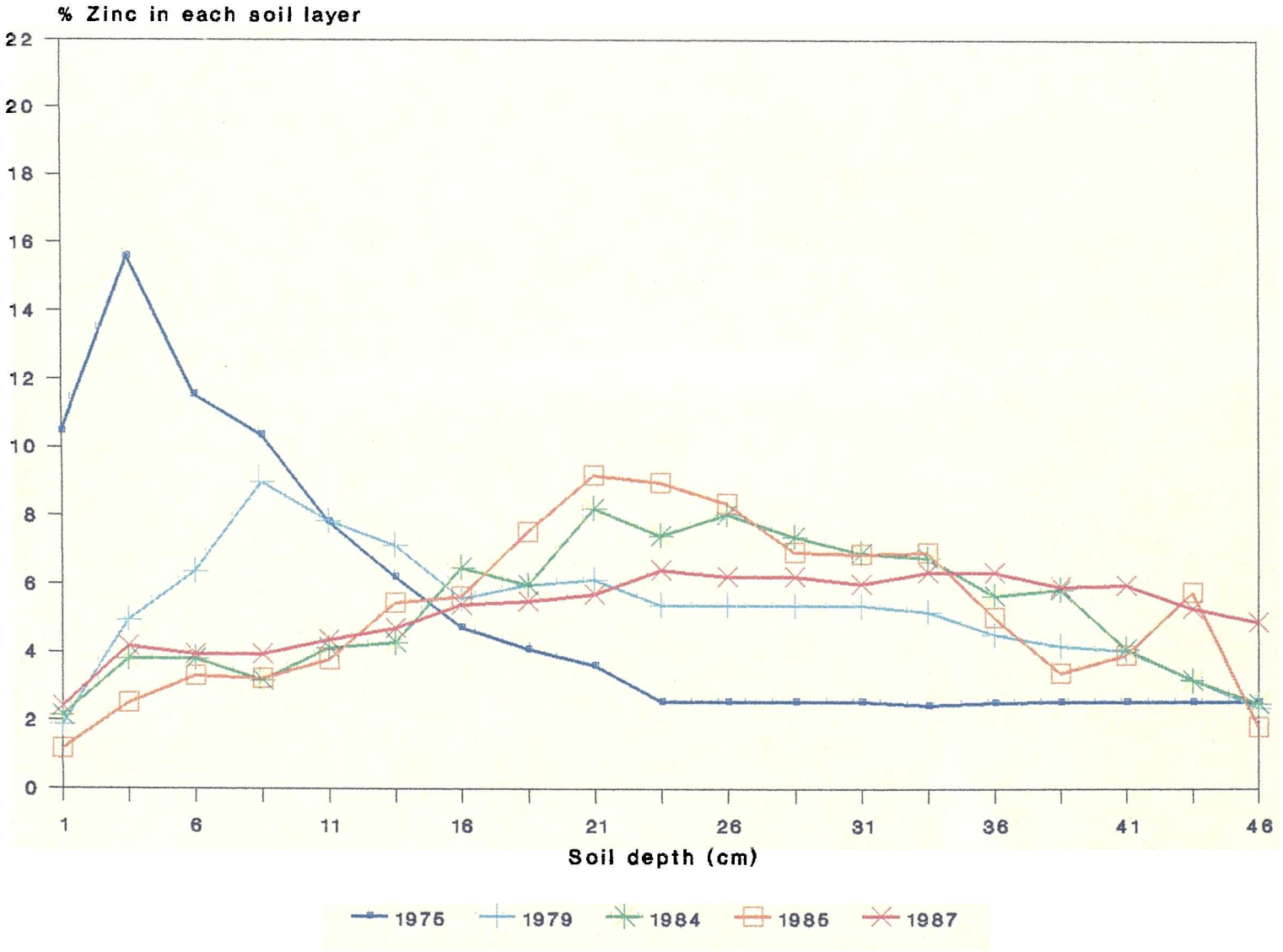


Fig.2.3.8b Hallen Wood Zinc

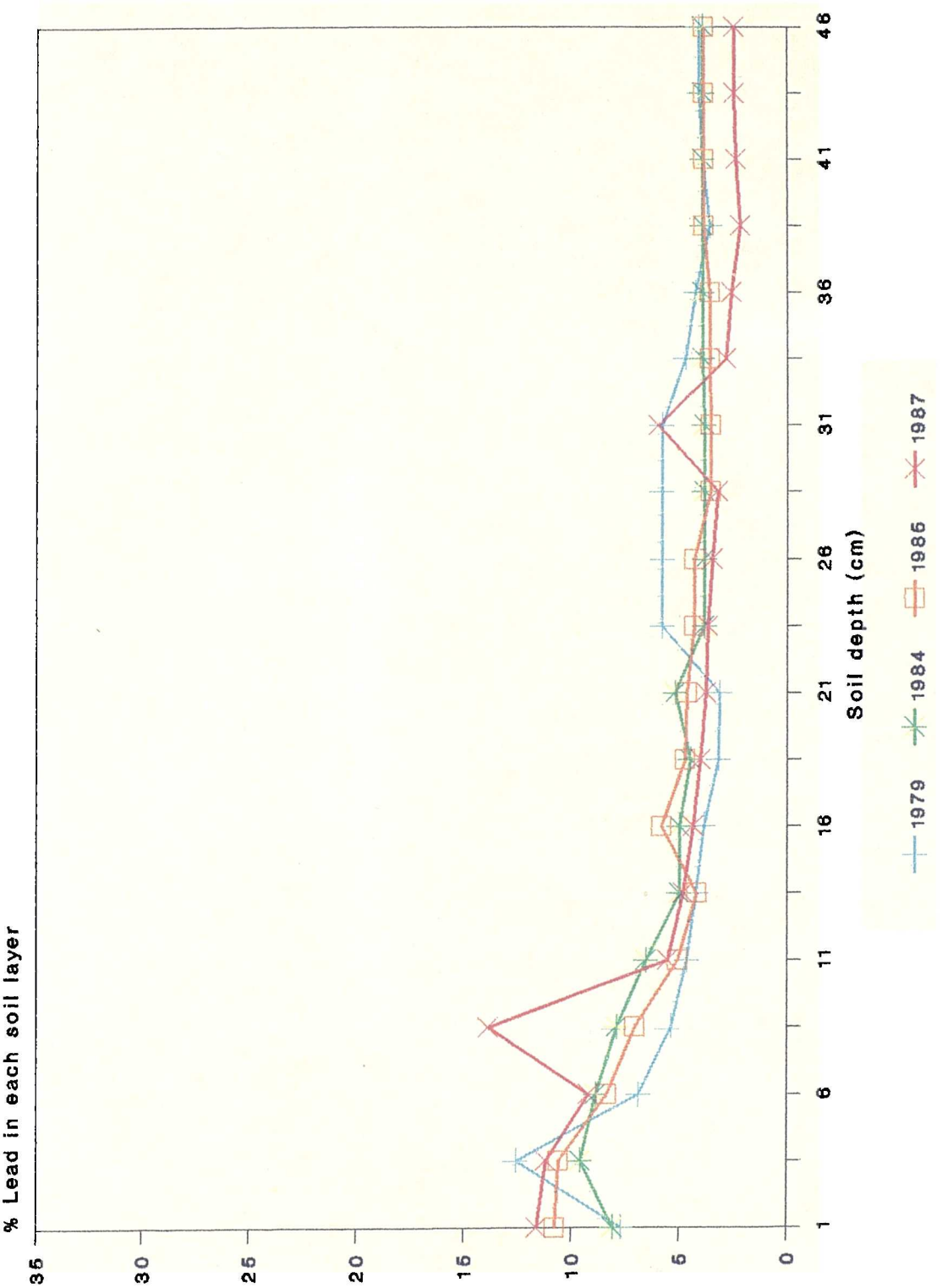


Fig.2.3.9a Haw Wood Lead

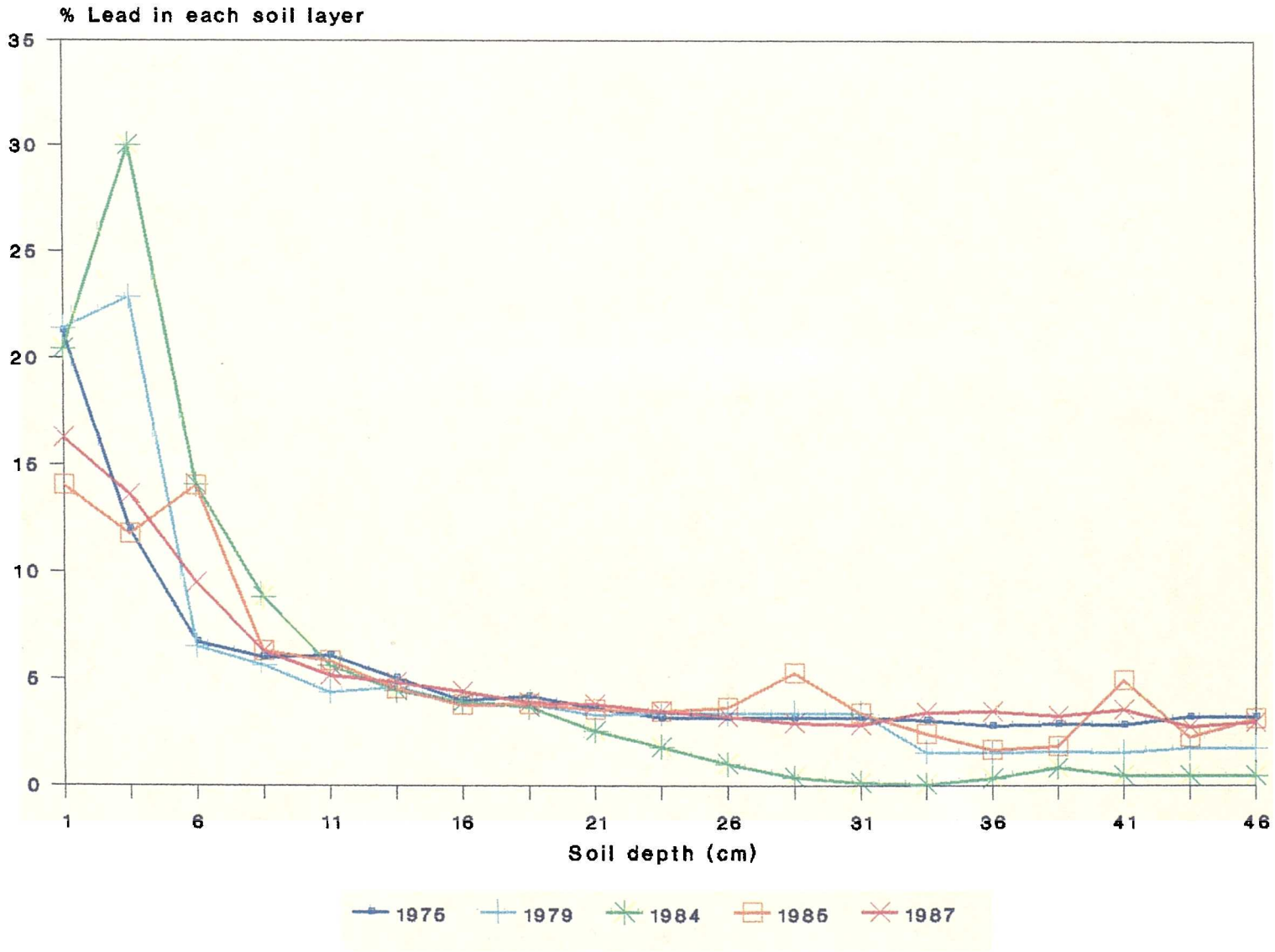


Fig.2.3.9b Hallen Wood Lead

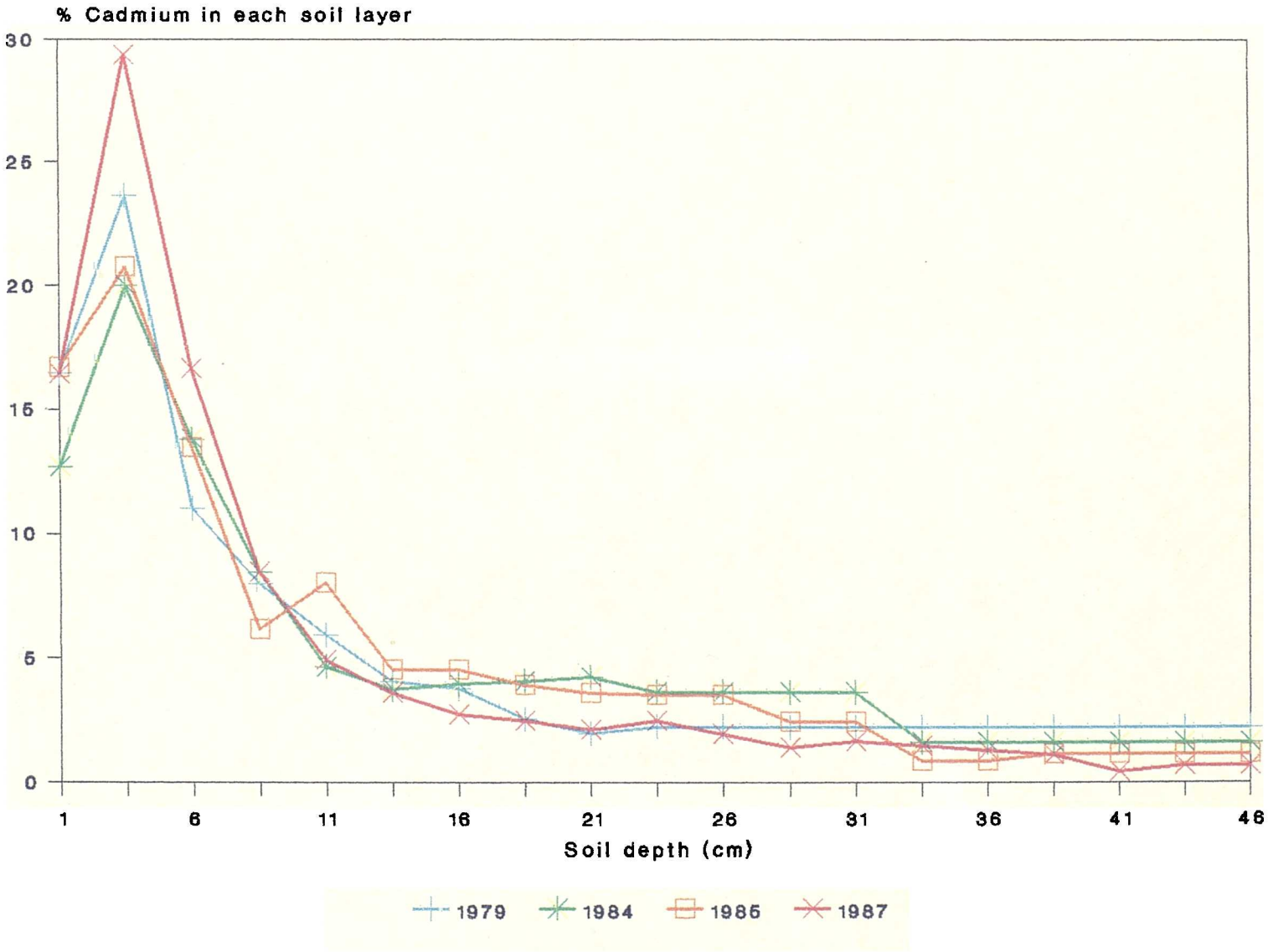


Fig.2.3.10a Haw Wood Cadmium

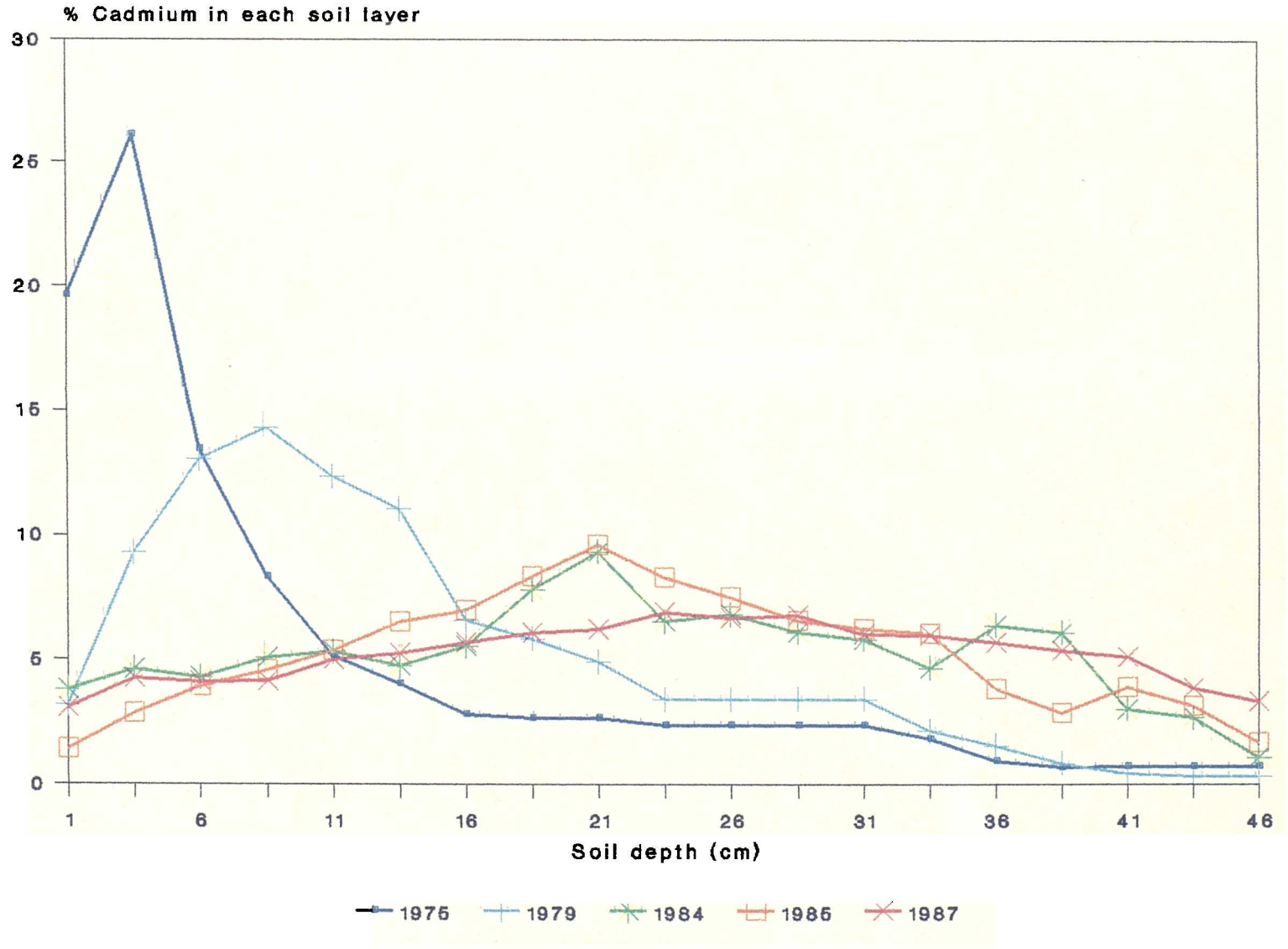


Fig.2.3.10b Hallen Wood Cadmium

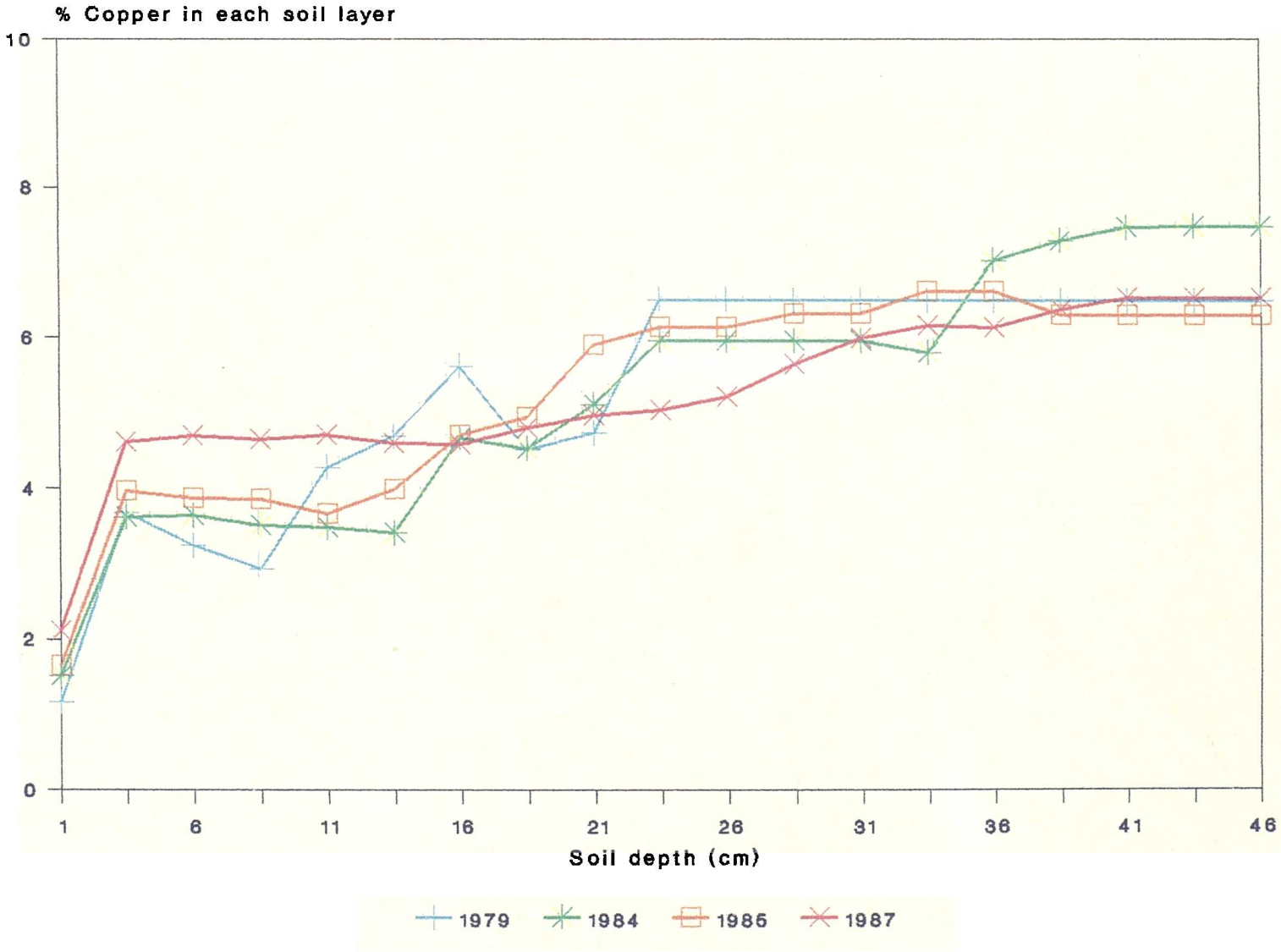


Fig.2.3.11a Haw Wood Copper

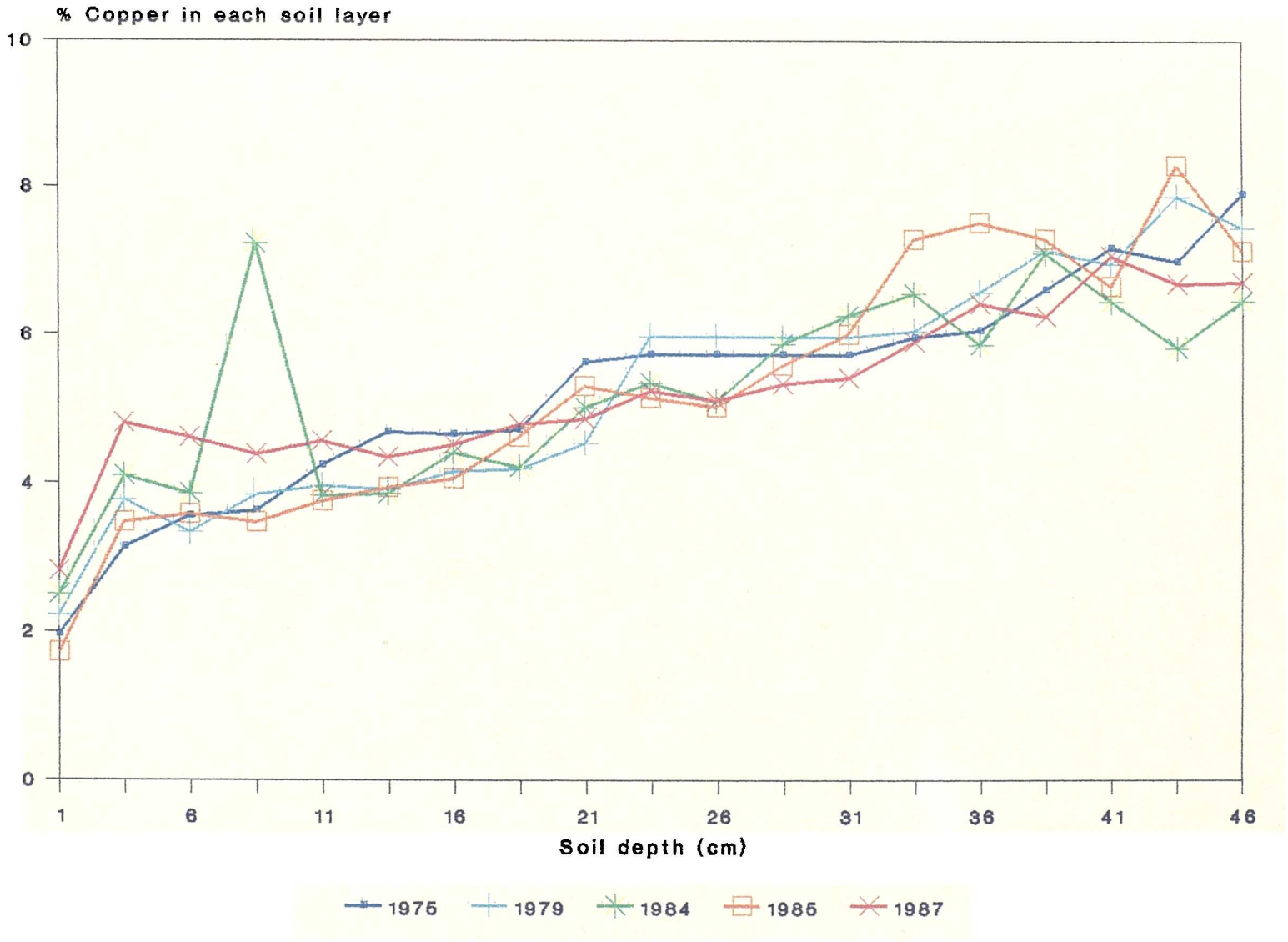


Fig.2.3.11b Hallen Wood Copper

Fig.2.3.12. Soil pH in Haw and Hallen Wood Soil Profiles (a=Haw, b=Hallen).

Fig.2.3.13. The Base Status of the 1987 Haw and Hallen Wood Soils.

Fig.2.3.14. Organic Matter in Haw and Hallen Wood Soils of Profiles Sampled during the 1980's.

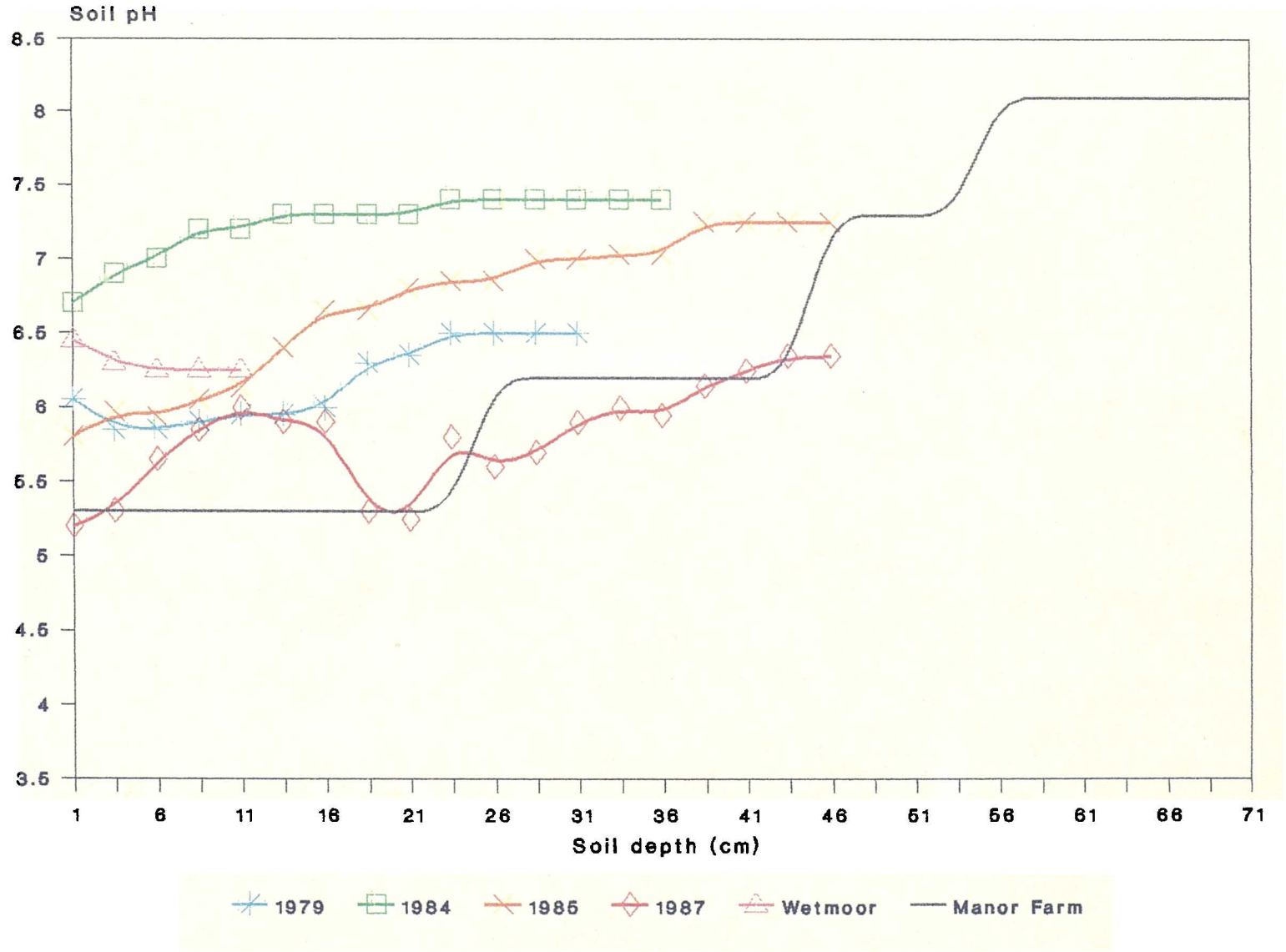


Fig.2.3.12a Haw Wood Soil pH

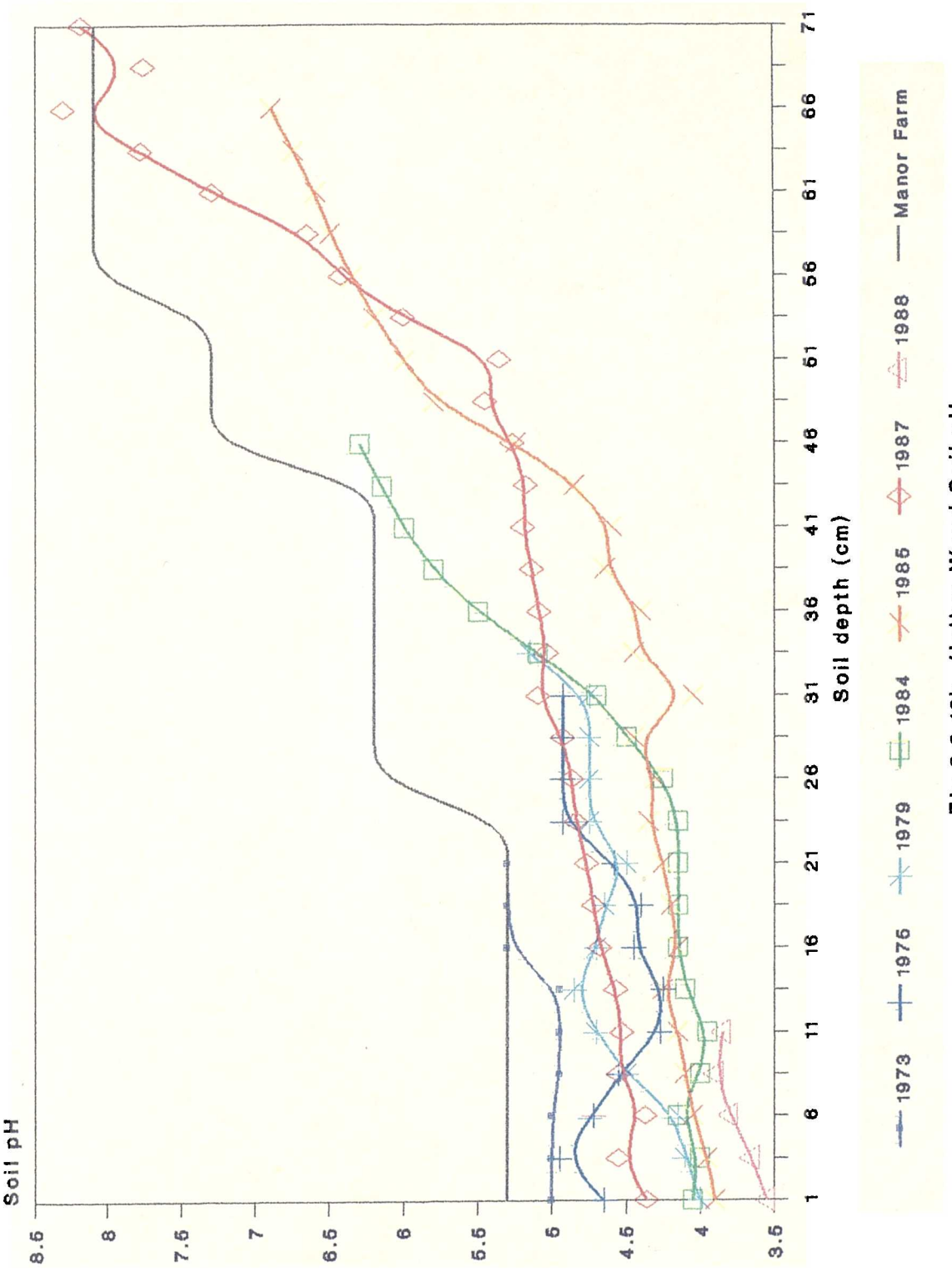


Fig.2.3.12b Hallen Wood Soil pH

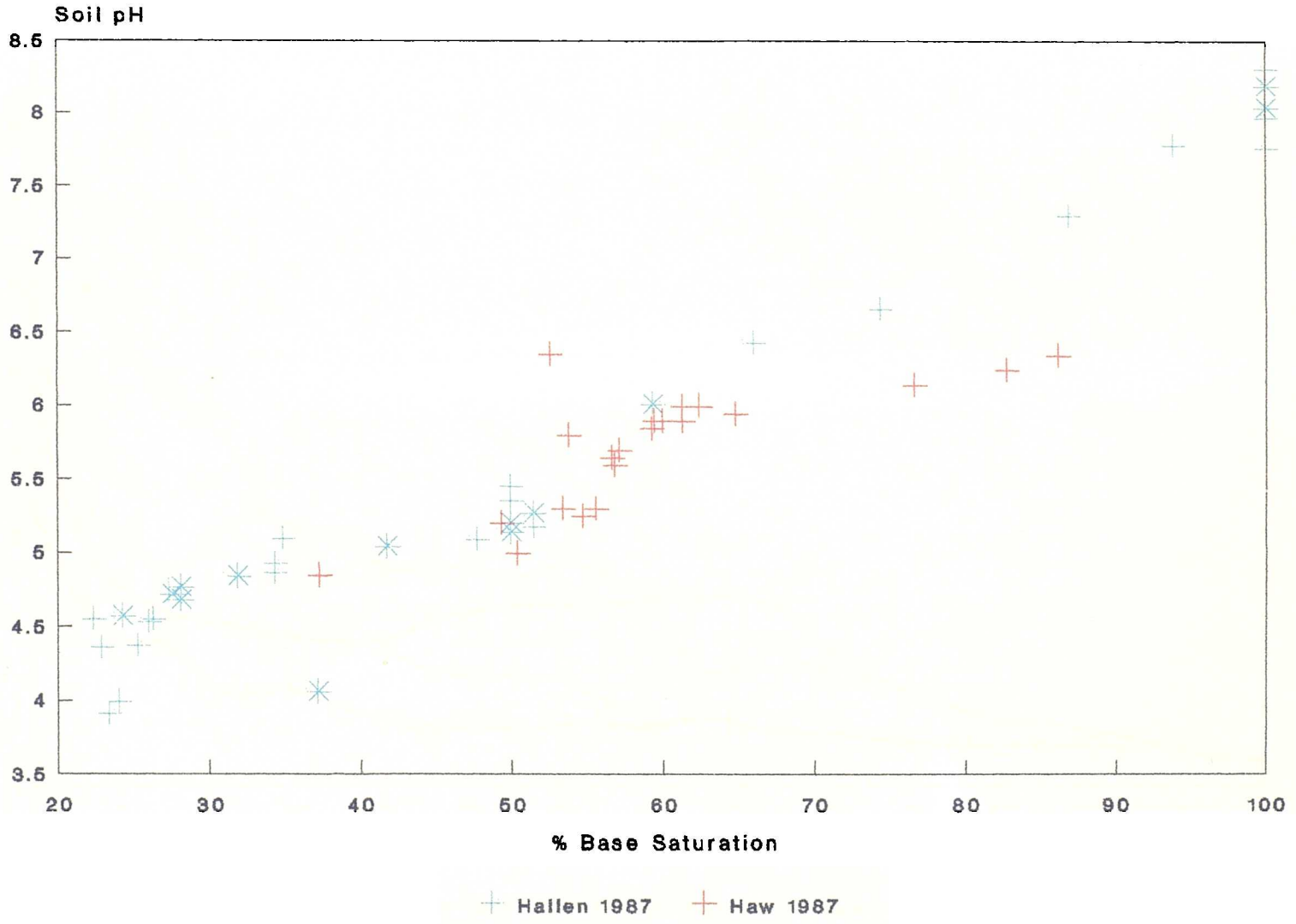


Fig.2.3.13 Base Status of Haw and Hallen Wood Soil Profiles

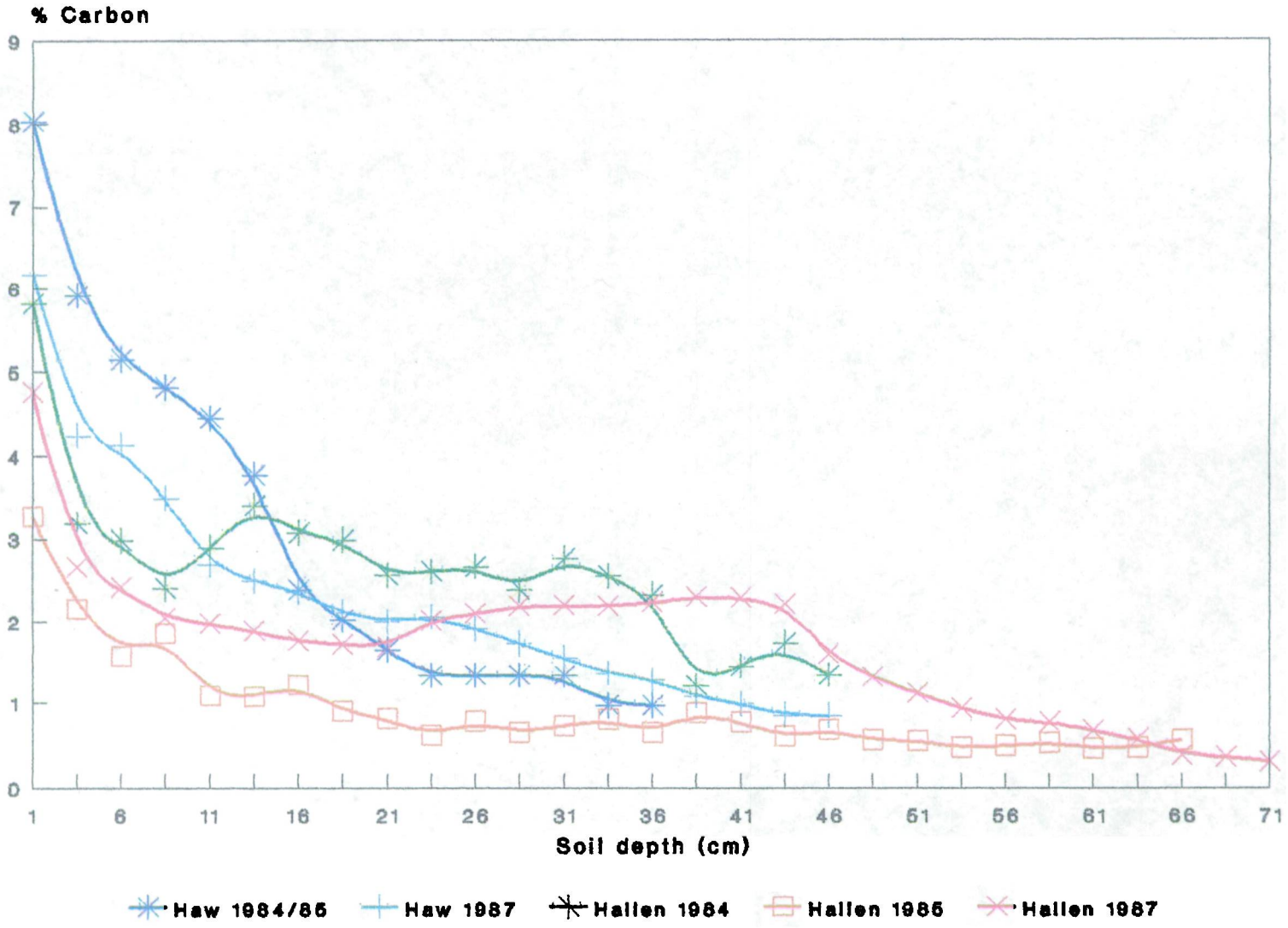


**Fig.2.3.14 Organic Matter in Haw and Hallen Wood Mineral Soil Profiles**

# CHAPTER THREE

# SOLID PHASE HEAVY METAL CHEMICAL EXTRACTION TECHNIQUES

# THE SEQUENTIAL EXTRACTION OF HEAVY METALS

## 3.1. Introduction

Chemical extractants have been used throughout this century primarily to determine the availability of nutrients in soil in relation to plant growth. Commonly employed extractants such as normal ammonium acetate at pH7 and 2.5% acetic acid were first introduced in the late 1920's by Schollenberger (1927) and Williams (1928) respectively. Extraction procedures were first used in pedology to assess the availability of trace substances important for soil fertility (Jackson 1958). The latter half of this century has heralded the age of environmental concern as regards heavy metal pollution in soils and sediments, and national and international guide-lines have been introduced to keep a check on metal levels. Guide-lines such as those for sludge applications on agricultural land (first introduced in the 1970's) normally specify maximum allowable total metal concentrations and exhibit considerable variation from one country to another (Lake *et al.*1984). The total analysis of heavy metals in soils provides useful information about metal enrichment in the soil or whether a maximum acceptable value of a metal has been exceeded. However, what is not always clear from total analysis is:

(a) The geochemical mobility of the metal in the soil.
(b) The bioavailability (and potential toxicity) of the metal to plants and other organisms.

Chemical extraction procedures have therefore evolved to account for the metal species found on solid phases of soils, sludges, sediments etc. By assessing the non-residual fractions of metals in solid phase materials a prognosis can be made as to the potential reservoir of metals available for release into any interstitial or surface water in contact with that solid phase. From this, the "availability" of the metal for mobility and biological uptake can be predicted.

## Table 3.1.1 Possible Approaches for the Determination of Metal Partitioning in Soils and Sediments (after Campbell and Tessier 1987)

1. Mathematical Modelling
   - thermodynamic equilibrium calculations (thermodynamic data not yet complete).

2. Experimental Manipulation
   - physical separation : grain size
     specific gravity
     magnetic properties
   - chemical separation : selective extractions

The Frequency (x) of separation methods used for differentiation of the bulk concentration of metals into physico-chemically defined fractions at the 1985 Athens 5th International Conference on Heavy Metals in the Environment (after Reuther 1987) :

| | | |
|---|---|---|
| 1. | Chemical extraction | 27x |
| 2. | Ion-exchange and gel chromatography | 13x |
| 3. | Gas chromatography | 10x |
| 4. | Mechanical (filtration, centrifugation, sieving) | 9x |
| 5. | Solvent extraction | 8x |
| 6. | HPLC chromatography | 3x |

Also :

Catechol violet
EDTA and batho phenanthroline complexation
Chemical modelling
Density and magnetic separation
Sorption experiments

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Other forms of metal partitioning / fractionation processes are feasible (see Table 3.1.1); but the best approach to speciation currently available depend on sequentially dissolving major fractions of a soil, sediment etc., and measuring the heavy metal released during each sequential stage (Harrison 1987).

## 3.2. Chemical Extraction Methodology

Heavy metals may be associated with various phases within soils:

(a) Metals dissolved, complexed, bound etc. in solution phase.

**Table 3.2.1 The Classification of Metals Associated with Soils, Sediments and Deposited Dusts (after Harrison *et al* 1981)**

| | Classification | Form of Association | Extraction Technique |
|---|---|---|---|
| 1. | Soluble | Metal precipitate; pore water | Release to pore water or river water |
| 2. | Exchangeable | Specifically adsorbed, exchangeable | Exchange with excess cations |
| 3. | Carbonate phase | Precipitate or co-precipitate | Release by mild acid |
| 4. | Fe-Mn oxide phase | Specifically adsorbed, co-precipitated | Reduction |
| 5. | Organic phase | Complex, adsorbed | Oxidation |
| 6. | Residual | In mineral lattices | Digestion with strong acids |

---

(b) Adsorbed at particle surfaces (e.g. clays, humic acids, metal oxyhydroxides).

(c) Precipitated as discrete metal compounds (e.g. carbonates, phosphates) or co-precipitated as a carbonate phase etc.

(d) Co-precipitation/occlusion of metals as discrete nodules, cement between particles, coatings on particles etc. of iron / manganese oxyhydroxides.

(e) Metals bound to organic molecules associated with detrital living forms.

(f) Sulphide-bound (amorphous or crystalline forms).

(g) Isomorphically substituted / matrix bound forms (clay, oxide, sulphide etc. lattice positions).

A schematic representation of metal partitioning in the soil environment is illustrated by Fig.3.2.1. The differentiation between the solution and solid phases will depend very much on the method of separation of the components (e.g. the physical mesh of the filter system employed).

There are a number of sequential extraction schemes that have been designed to separate the metal species associated with various solid phases, although the availability of "selective reagents" is very limited and only a partial separation can be achieved (Harrison 1987). The principle behind, and the purpose of chemical extraction sequences is demonstrated in Table 3.2.1.

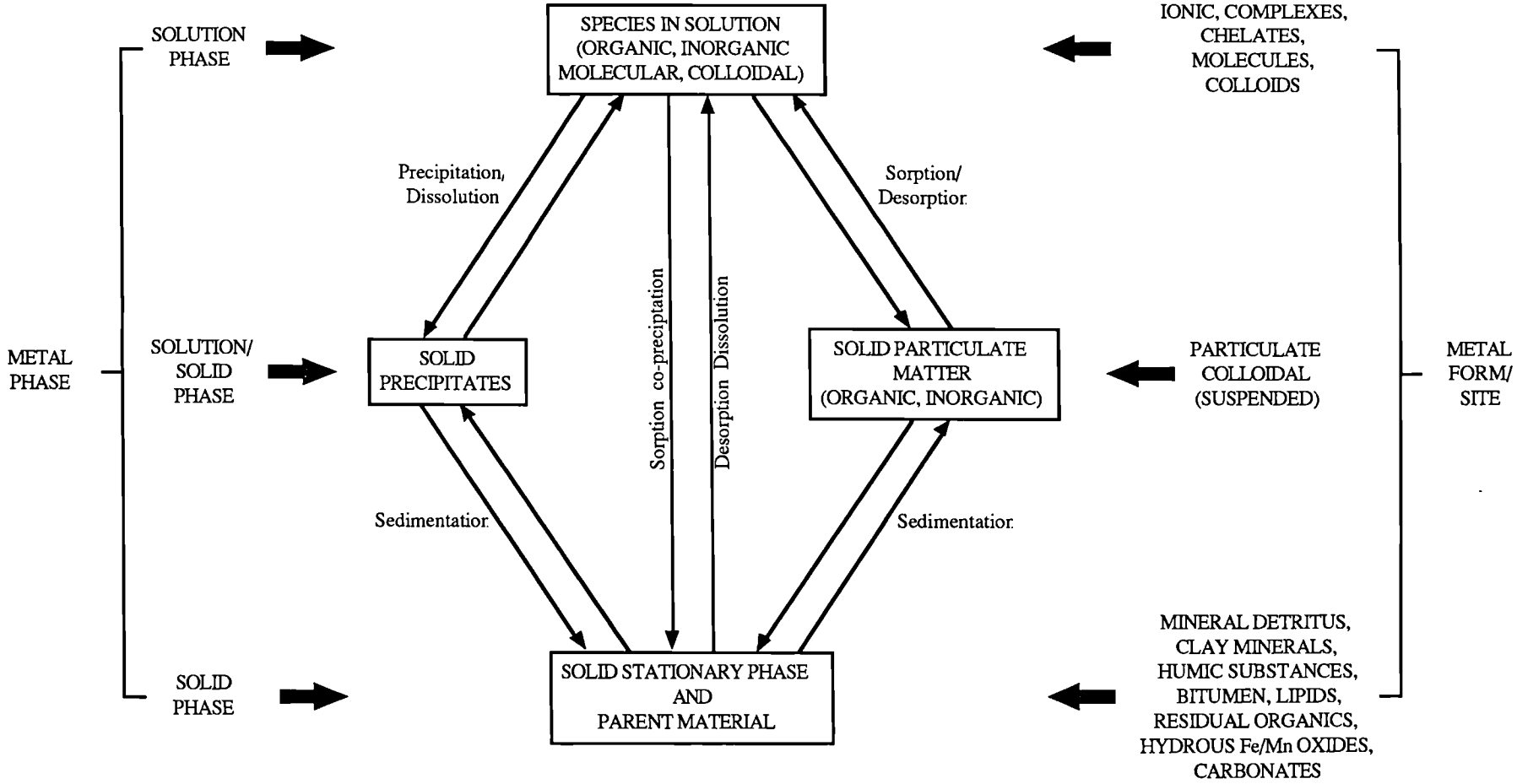


Fig 3.2.1 Distribution of a Trace Element Between Solid and Solution Phases

**Table 3.3.1 Examples of Extracting Agents used to Fractionate Heavy Metals in Soils and Sediments. (This Table is continued on page 108).**

| | | |
|---|---|---|
| Soluble : | | |
| | $H_2O$ | |
| Exchangeable Phases : | | |
| | $NH_4^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ Chlorides/Nitrates (Neutral salts) | - |
| * | $MgCl_2$, pH7 | Gibbs (1973) |
| * | $BaCl_2$ - TEA, pH8.1 | Jackson (1958) |
| * | $NH_4OAc$, pH7 | Engler *et al.*(1977) |
| | LiCl + CsCl (in 60% $CH_3OH$) | Lum & Edgar (1983) |
| | NaOAc, pH6.5 | Khalid *et al.*(1978) |
| Specifically Adsorbed/Carbonate/Chelated Phases : | | |
| + | $Pb(NO_3)_2$ | Ramamoorthy & Rust (1978) |
| + | HOAc | McLaren & Crawford (1973) |
| | KF | Stover *et al.*(1976) |
| + | EDTA | Bloomfield & Pruden (1975) |
| | CuOAc | Boust & Saas (1981) |
| | DPTA | Silviera & Sommers (1977) |
| * | NaOAc/HOAc, pH5 | Tessier *et al.*(1979) |
| * | Acidic cation exchanger | Deurer *et al.*(1978) |
| * | $CO_2$ treatment of suspension | Patchineelam (1975) |
| Reducible/Oxide Phases : | | |
| * | $NH_2OH.HCl$ (+ $HNO_3$) | Chao (1972) |
| * | Ammonium oxalate buffer (dark/U.V.) | Schwertmann (1964) |
| * | Hydroxylamine-acetic acid | Chester & Hughes (1967) |
| ‡ | Dithionite-citrate buffer | Mehra & Jackson (1960) |

Organic Fraction (including sulphides) :

| | | |
|---|---|---|
| +* | NaOH | Rashid and King (1971) |
| + | Pyrophosphate-K | Bascomb (1968) |
| + | NaOCl | Anderson (1963) |
| + | $CH_3COCH_2COCH_3$ | Hamblin and Posner (1979) |
| * | $H_2O_2$-$NH_4OAc$, pH2.5 | Engler *et al.*(1977) |
| # | Pyrophosphate-Na | Stover *et al.*(1976) |
| + | $H_2O_2$-NaOAc | Jackson (1974) |
| +* | $H_2O_2$-$HNO_3$ | Gupta and Chen (1975) |
| * | $NaOH/H_2SO_4$ | Volkov and Fomina (1974) |
| # | DPTA-NaOAc, pH7 | Khalid *et al.*(1981) |
| § | Bromoethanol | Nelson *et al.*(1966) |
| * | Organic solvents | Cooper and Harris (1974) |

After :

| | |
|---|---|
| * | Salomons and Förstner (1980) |
| + | Miller *et al.*(1986) |
| +* | Förstner (1983) |
| # | Tessier and Campbell (1987) |
| ‡ | Shuman (1982) |
| § | Guy *et al*,(1978) |

---

## 3.3. The Choice of Chemical Extractant Reagent

There are a wide variety of different reagents that may be used to extract heavy metals from a particular soil phase or component (see Table 3.3.1). The variety of extractants available has been reviewed by numerous authors e.g. Brümmer (1986), Davies (1983), Förstner (1982, 1983, 1985), Guy *et al.* (1978), Miller *et al.* (1986), Shuman (1982), Tessier and Campbell (1987). Examples of extractants used in soils and sediments are shown in Fig.3.3.1 (after Pickering 1981). Fig.3.3.1 illustrates the various efficiencies with which extractants remove metals from different soil phases. A study by Luoma and Bryan (1981) demonstrated the efficiency of varying reagents in the extraction of metals from oxic estuarine sediments (see Table 3.3.2). Even concentrated strong acids such as nitric acid may not be altogether 100% efficient at extracting all the metal (Hall and Chang-Yen 1989).

In general, extractants fall into one of the following groups (Campbell and Tessier 1987):

(a) Concentrated inert electrolytes (desorption of electrostatically adsorbed metals).

(b) Weak acids (dissolution of carbonate phases; desorption of specifically adsorbed metals).

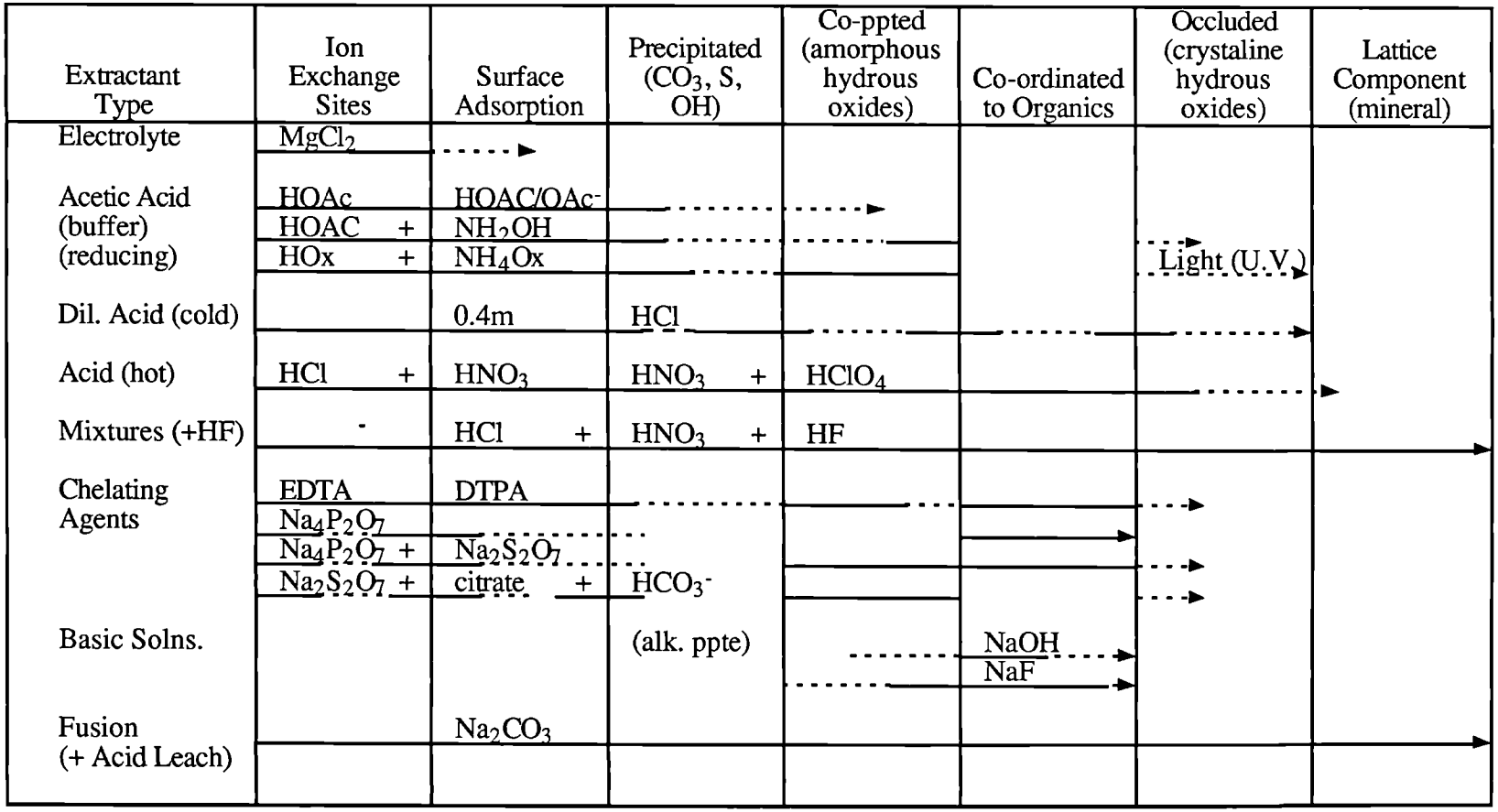


Fig.3.3.1 Schematic Representation of the Ability of Different Extraction Solutions to Release Metal Ions Retained in Different Modes or Associated with Specific Soil and Sediment Fractions (from Pickering (95), CRC Crit.Rev.Anal.Chem., Nov. 1981)

Dashed segments indicate areas of uncertainty.

**Table 3.3.2 The Percentage of Total Metal Extracted by Various Extractants (after Luoma and Bryan 1981)**

| Extractants | Cu | Pb | Zn |
|---|---|---|---|
| 1. Conc. $HNO_3$ | 100 | 100 | 100 |
| 2. 1M HCl | 64.6 | 72.2 | 63.7 |
| 3. 25% HOAc | 47.8 | 46.8 | 60.1 |
| 4. 0.2M $(NH_4)_2C_2O_4$ + 0.2M $H_2C_2O_4$, pH3.3 | 31.3 | 21.6 | 53.8 |
| 5. 0.1M $NH_2OH.HCl$ in 0.01M $HNO_3$, pH2 | 24.4 | 35.8 | 40.4 |
| 6. 1M $NH_4OAc$, pH7 | 2.5 | 3.8 | 5.9 |
| 7. 0.1M $Na_4P_2O_7$ | 5.1 | 6.3 | 15.5 |
| 8. 1M $NH_3$ | 0.46 | - | - |
| 9. 0.1M NaOH | 0.64 | - | - |

---

(c) Reducing agents (reduction of amorphous iron and/or manganese oxyhydroxides).

(d) Complexing agents (competition for metals complexed with organic functional groups; dissolution of precipitates).

(e) Oxidising agents (oxidation of organic matter and sulphides).

(f) Strong mineral acids (dissolution of resistant oxides, sulphides and aluminosilicates).

(g) Alkali solubilisation of humic and fulvic acids e.g. NaOH.

The biologically active metal fractions found in the soil are the soluble, exchangeable and complexed forms. Extraction solutions with the best requirement for correlation with plant uptake should meet the following criteria (Kiekens and Cottenie 1985):

(a) Be sufficiently acid to solubilise a solid phase fraction which contributes to plant uptake.

(b) Contain a displacing ion in order to exchange a fraction of adsorbed ions.

(c) Have the property to extract soluble organo-mineral complexes.

Based on these considerations, the FAO European Cooperative Network proposed a reference method using 0.5M $NH_4OAc$ + 0.02M EDTA, pH4.65 as an extracting solution; but a single extraction can only reflect the situation for a given moment - no information is provided about the effects to be expected over a longer period of time. By using a number of extractants with increasing

**Table 3.3.3 The Proportions of Cadmium Extracted by Seven Extractants from Three Soils**

| Soil pH | Sequences of Proportions of Cd Extracted |
|---|---|
| pH5.0 | $CaCl_2$ (= $NH_4Cl$ >) » $Ca(NO_3)_2$ = $Ca(AcO)_2$ = 1N $NH_4OAc$ = $KNO_3$ = $NH_4OAc$ |
| pH7.0 | $CaCl_2$ » $Ca(OAc)_2$ = 1N $NH_4OAc$ (= $NH_4Cl$ =) » $Ca(NO_3)_2$ = $NH_4OAc$ > $KNO_3$ |
| pH7.6 | $CaCl_2$ = 1N $NH_4OAc$ » $Ca(OAc)_2$ = $NH_4Cl$ (= $NH_4OAc$ =) » $Ca(NO_3)_2$ = $KNO_3$ |

1. The concentration of all extractants, except 1N $NH_4OAc$ as indicated in the Table, is 0.5N
2. » the more significant differences
   > differences outside the experimental error (CV 5%)
   = no significant differences

---

aggressivities (either individually or sequentially) then some quantitative measure can be made about the amount of metal that may be made available in the future (e.g. due to a reduction in soil pH).

There are a great number of different extraction techniques available. As yet there is no "universal method" employed for either assessing the availability or the partial separation of heavy metals in soils. For example the exchangeable fractions of metals in soils may be assessed by the use of 1M $NH_4OAc$, pH7. Studies which have examined the availability of heavy metals and plant uptake might utilise this extractant (e.g. Jones *et al.*1981, Kiekens and Cottenie 1983). However other salts are available for assessment of exchangeable metals e.g. Brümmer (1986) recommended neutral salt solutions, in particular 0.1M $Ca(NO_3)_2$ or $CaCl_2$. In an assessment of seven different extractant treatments, Zhan (1986) found that $CaCl_2$ was the most efficient extractant for cadmium from three different soils (Table 3.3.3). Neutral salts such as 0.1M $NaNO_3$ (Hani and Gupta 1985) and 0.1M $CaCl_2$ (Sauerbeck and Styperek 1985) reflect actual availabilities of metals in soils for plant uptake. $CaCl_2$ is a useful salt to use because it (Sauerbeck and Styperek 1985):

(a) reflected soil type dependent differences in availability.
(b) reflected the modifying influence of the particular source.
(c) reflected the modifying influence of the soil pH.

(d) closely correlated with plant uptake.

The choice and effectiveness of an extractant as related to plant availability is often based on empiricism and extractants such as 2.5% HOAc or 0.05M EDTA have often been used for this purpose (Jarvis 1977). Thus in their choice of reagents for assessment of available cadmium in agricultural soils in England and Wales, Jarvis and Jones (1980) used 0.002M $CaCl_2$, 0.05M $CaCl_2$, 0.42M HOAc and 0.05M EDTA (pH7). Likewise Archer and Hodgson (1987) in their survey of trace elements in soils of England and Wales employed 0.5M HOAc and 0.05M EDTA (see also Chapter 5 Section 1 for further details about chemical extractants and plant uptake).

## 3.4. Heavy Metal Partitioning Determined by Chemical Extractions

Reagents that can be used in partitioning sequences or sequential extractions in order to assess solid phase metal species should fall into the categories mentioned in Section 3.3 (Campbell and Tessier 1987). Many of the sequences developed have been used to assess metal availability in soils, sediments, sludges, deposited dusts, fly ash etc. There are a multitude of different extraction sequences that can be chosen. Perhaps the most revolutionary extraction sequence that has been developed was that created by Tessier *et al.*(1979). It bears a close lineage to the sequence advocated by Salomons and Förstner (1980) and has been used throughout the 1980's. From the literature available, there would appear to be three important extraction sequences which other sequences have developed from or bear close resemblance to. The three extraction schemes of McLaren *et al.*(1973), Stover *et al.* (1976), Tessier *et al.* (1979), and related schemes are shown in Table 3.4.1, Table 3.4.2 and Table 3.4.3. Nearly all the fractionation schemes mentioned are sequential extractions. The scheme devised by McLaren and Crawford (1973) is a two phase sequential extraction where steps 1 and 2 are carried out independently of 3, 4 and 5.

Other reports worthy of note where sequential extraction sequences have been devised are those of Shuman, Gibbs (1973), Miller and co-workers, and Khalid, Patrick, Gambrell and co-workers. Examples of these schemes are shown in Table 3.4.4. Other sequential extraction sequences used include Badri and Aston (1981), Boust and Saas (1981), McNeal *et al.* (1985), Meguellati *et al.*(1981) and Legret *et al.*(1983). Other fractionation schemes

**Table 3.4.1 McLaren and Crawford (1973 a, b and 1974) and Related Extraction Techniques**

| Extractants | Fraction Extracted | Reference |
|---|---|---|
| 1. 0.05M $CaCl_2$ | Soluble/Exchangeable | McLaren & Crawford (1973 a,b) |
| 2. 2.5% HOAc | Specifically adsorbed | McLaren & Crawford (1974) |
| 3. 1.0M $K_4P_2O_7$ | Organically bound | Garcia-Miragaya (1981) |
| 4. 0.1M $H_2C_2O_4$ + 0.175M $(NH_4)_2C_2O_4$, pH3.25 | Mn/Fe oxide occluded | Payne *et al.*(1988) Elsokkary & Låg (1978) |
| 5. HF | Residual | Garcia-Miraagaya *et al.*(1981) |
| 1. $H_2O$ | Soluble | Martin *et al.*(1976) |
| 2. 0.1M $NH_4NO_3$ | Weakly exchangeable | Coughtrey (1978) |
| 3. 0.1M $CaCl_2$ | Exchangeable | |
| 4. 2.5% HOAc | Specifically adsorbed | |
| 5. 0.2M NaOH | Organically bound | |
| 6. $HNO_3$ (conc.) | Residual | |
| 1. 1M KCl | Soluble/Exchangeable | Stevenson (1979) |
| 2. 2.5% HOAc | Specifically adsorbed | |
| 3. 0.15M $Na_4P_2O_7$ (or 20% $H_2O_2$) | Organically bound | |
| 4. HF : HCl | Residual | |

**Table 3.4.1 (cont.)**

| | | |
|---|---|---|
| 1. 0.05M $CaCl_2$ | Soluble/Exchangeable | Iyengar *et al.*(1981) |
| 2. 2.5% HOAc | Specifically adsorbed | Mullins *et al.*(1982 a, b) |
| 3. 0.1M $K_4P_2O_7$ | Organically bound | |
| 4. 0.1M $NH_2OH.HCl$ + 0.01M $HNO_3$ | Mn/Fe (amorph.) oxides | |
| 5. 0.1M $H_2C_2O_4$ + 0.175M $(NH_4)_2C_2O_4$ (U.V.) | Fe (cryst.) oxides | |
| 6. HF-HCl-$HNO_3$ | Residual | |
| 1. $H_2O$ | Soluble | Alloway *et al.*(1979) |
| 2. 0.05M $CaCl_2$ | Exchangeable | |
| 3. 0.1M $K_4P_2O_7$ | Organically bound | |
| 4a. 0.2M $(NH_4)_2C_2O_4$ pH3.3 (for copper) | Fe/Mn oxide occluded | |
| b. 0.1M $NH_2OH.HCl$, pH2 + citrate-dithionite pH3.8 (for Pb and Cd) | Fe/Mn oxide occluded | |
| 5. $HNO_3$ (conc.) | Residual | |

**Table 3.4.2 Stover *et al* (1976) and Related Extraction Techniques**

| Extractants | Fraction Extracted | Reference |
|---|---|---|
| 1.1M $KNO_3$ | Soluble/Exchangeable | Stover *et al.*(1976) |
| 2.0.5M KF | Specifically adsorbed | Schalscha *et al.*(1980) |
| 3.0.1M $Na_4P_2O_7$ | Organically bound | Schalscha *et al.*(1982) |
| 4.0.1M EDTA | Carbonate | |
| 5.1M $HNO_3$ | Sulphide | |
| 1.0.5M $KNO_3$ | Soluble/Exchangeable | Chang *et al.*(1984) |
| 2.Deionised $H_2O$ (x3) | Specifically adsorbed | Emmerich *et al.*(1982a) |
| 3.0.5M NaOH | Organically bound | Sposito *et al.*(1982) |
| 4.0.05M EDTA | Carbonate | Sposito *et al.*(1983) |
| 5.4M $HNO_3$ | Sulphide/Residual | |
| 1.$H_2O$ | Soluble | Miller *et al.*(1983) |
| 2.1M $KNO_3$ | Exchangeable | Miller & McFee (1983) |
| 3.0.5M $NH_4F$ | Specifically adsorbed | |
| 4.0.1M $Na_4P_2O_7$ | Organically bound | |
| 5.0.1M EDTA, pH7 | Carbonate | |
| 6.0.1M $NH_2OH.HCl$, pH3 | Mn/Fe (amorph.) oxides occluded | |
| 7.Citrate-bicarbonate-dithionite | Fe (cryst.) oxides | |
| 8.1M $HNO_3$ | Precipitated metals | |
| 9.$HNO_3$ (conc.) | Residual | |

See also : Silviera & Sommers (1977)
Petruzzelli *et al.* (1981a)
Petruzzelli *et al.* (1983)

**Table 3.4.3 Tessier *et al* (1979) and Related Extraction Techniques**

| Extractants | Fraction Extracted | Reference |
|---|---|---|
| 1. 1M $MgCl_2$, pH7.0 (or 1M $NH_4OAc$) | Sobluble/Exchangeable | Tessier *et al.*(1979 a, b; 1980; 1982)<br>Harrison *et al.*(1981) |
| 2. 1M NaOAc, pH5 | Carbonate | Lion *et al.*(1982) |
| 3. 0.04M $NH_2OH.HCl$ 25% HOAc (or Citrate-dithionite) | Fe/Mn oxide occluded | Lum & Edgar (1983)<br>Dominik *et al.*(1983)<br>Rapin & Förstner (1983)<br>Reuther *et al.*(1983) |
| 4. 30% $H_2O_2$ +0.02M $HNO_3$ (x2) (3.2M $NH_4OAc$ + 20% $HNO_3$) | Organically bound | Bradley & Cox (1987)<br>Xian (1987)<br>Xian & Shokohifard (1989) |
| 5. HF-$HClO_4$ | Residual | Belzile *et al.*(1989)<br>Hickey & Kittrick (1984)<br>Xian (1989) |
| 1. 1M $NH_4OAc$, pH7 | Soluble/Exchangeable | Salomons & Förstner (1980) |
| 2. 0.1M $NH_2OH.HCl$ + 0.01M $HNO_3$ | Mn/Fe (amorph.) oxide occluded | Förstner *et al.*(1981)<br>Reuther *et al.*(1981) |
| 3. 0.2M $(NH_4)_2C_2O_4$ + 0.2M $H_2C_2O_4$ | Fe (cryst.) oxide occluded | Förstner (1982)<br>Angelidis & Grimanis (1989) |
| 4. 30% $H_2O_2$, pH2 (1M $NH_4OAc$) | Organically bound | |
| 5. $HNO_3$ (conc.) | Residual | |

**Table 3.4.3 (cont.)**

Others :

| | | |
|---|---|---|
| 1. $NH_4OAc$ (or $MgCl_2$) | Soluble/Exchangeable | Engler *et al.*(1977) |
| 2. $NH_2OH.HCl$ ($HNO_3$) | Mn/Fe (amorph.) oxides | Lindau & Hossner (1982) |
| 3. $H_2O_2$ ($HNO_3$) | Organic (+ sulphide) | |
| 4. Dithionite | Fe (cryst.) oxides | Gupta & Chen (1975) |
| 5. HF-$HNO_3$ ($H_2SO_4$) | Residual | Kitano & Fujiyoshi (1980) |
| | | |
| 1. $NH_2OH.HCl$ ($HNO_3$) | Easily reducible | Chao & Theobald (1976) |
| 2. $NH_2OH.HCl$ (HOAc) | Easily reducible | |
| 3. Dithionite | Moderately reducible | |
| 4. $KClO_4$ ($HCl/HNO_3$) | Organic | |
| 5. HF-$HNO_3$ | Residual | |

**Table 3.4.4 Other Extraction and Related Techniques**

| Extractants | Fraction Extracted | Reference |
|---|---|---|
| | Sims and Patrick (1978) | |
| 1. $H_2O$ | Water soluble | Sims & Patrick (1978) |
| 2. $H_2O$-complexed | Water soluble | Khalid *et al.*(1979) |
| 3. 1M NaOAc | Exchangeable | Gambrell *et al.*(1980) |
| 4. 1M $K_4P_2O_7$ | Specifically adsorbed | Khalid *et al.*(1978) |
| 5. 0.1M $NH_2OH.HCl$ + 0.01M $HNO_3$, pH2 | Mn/Fe (amorph.) oxide occluded | Khalid *et al.*(1981) |
| 6. 0.1M $H_2C_2O_4$ + 0.175M $(NH_4)_2C_2O_4$, pH3.5 | Fe (cryst.) oxide occluded | |
| 7. 0.5M NaOH | Organically bound | |
| 8. HF-$HNO_3$-$HClO_4$ | Residual | |
| | Shuman (1985) | |
| 1. 1M $Mg(NO_3)_2$, pH7 | Exchangeable | Shuman (1985) |
| 2. 0.7M NaOCl, pH8.5 | Organically bound | Shuman (1979) |
| 3. 0.1M $NH_2OH.HCl$ + 0.01M $HNO_3$, pH2 | Mn oxide occluded | Sims (1986) |
| 4. 0.2M $(NH_4)_2C_2O_4$ + 0.2M $H_2C_2O_4$, pH3 (dark) | Fe (amorph.) oxide occluded | |
| 5. 0.2M $(NH_4)_2C_2O_4$ + 0.2M $H_2C_2O_4$ + 0.1M ascorbic acid | Fe (cryst.) oxide occluded | |
| 6. HF-$HNO_3$-HCl | Residual (sand+silt+clay) | |

**Table 3.4.4 (cont.)**

Miller *et al* (1986)

| | | |
|---|---|---|
| 1. $H_2O$ | Soluble | Miller *et al.*(1985) |
| 2. 0.5M $Ca(NO_3)_2$ | Exchangeable | Miller *et al.*(1986 a, b) |
| 3. 0.05M $Pb(NO_3)_2$ | Specifically bound | |
| 4. 0.44M HOAc | Specifically bound | |
| 5. 0.1M $NH_2OH.HCl$, pH2 | Mn oxide occluded | |
| 6. 0.1M $K_4P_2O_7$, pH10 | Organically bound | |
| 7. 0.175M $(NH_4)_2C_2O_4$ + 0.1M $H_2C_2O_4$ (dark) | Fe (amorph.) oxide occluded | |
| 8. 0.175M $(NH_4)_2C_2O_4$ + 0.1M $H_2C_2O_4$ (U.V.) | Fe (cryst.) oxide occluded | |
| 9. $HF-HNO_3-HCl$ | Residual | |

Gibbs (1973)

| | | |
|---|---|---|
| 1. $H_2O$ | Water soluble | Gibbs (1973) |
| 2. 1N $MgCl_2$, pH7 | Exchangeable | Kuo *et al.*(1983) |
| 3. Citrate-dithionite | Fe/Mn oxide occluded | Shuman *et al.*(1978) |
| 4. NaOCl, pH8.5 | Organically bound | |
| 5. $HNO_3$ | Residual | |

**Table 3.4.5 Chemical Extraction Techniques Used for Metal Speciation (after Reuther 1987)**

| Extractants | Metal Species | Kind of Sample | Vol / Page |
|---|---|---|---|
| 1M $NH_4Ac$, pH4.8 | Sorbed/loosely bound metals | Fe-rich concretions<br>Spring water | I / 263<br>I / 266 |
| 1M $NH_2OH.HCl$ | Mn oxides | (Fe, Mn, Zn, Ca, Mg | |
| 1M $NH_2OH.HCl$ + 4M HAc | Hydrous Fe oxides | K, Si) | |
| 0.1M $Na_4P_2O_7$, pH11 | Organically bound metals | | |
| 6M HCl | Well ordered Fe oxides | | |
| 0.1M EDTA | Metal-humic acid compl. | Urban sludge | I / 336 |
| 0.01M HCl | Metals bound to humics | (Mn, Zn, Cu) | |
| 0.1M HCl | Metals bound to humics | | |
| 1M HCl | Metal oxides + humic complexes | | |
| Mn-hydroxide tetraborate, pH9.6 | Organo-mineral complexes | Soil matter<br>(Cd, Cu) | I / 342 |
| Na-pyrophosphate, pH9.7 | Organo-mineral complexes | | |
| Oxalate buffer, pH3.0 | Amorphous/crystallised Fe and Al oxyhydroxides | | |
| $NH_2OH.HCl$, acid | Reducible fraction | Marine sediments | I / 348 |
| $H_2O_2$, acid | Oxidisable fraction | (Fe, Cr, Zn) | |
| 25% HAc | Non-detrital phase | Ext. susp. part. matter<br>(Zn, Cu, Pb, Cd) | I / 380 |
| HF/aqua regia | Detrital phase | | |

**Table 3.4.5 (cont.)**

| | | | |
|---|---|---|---|
| HAc<br>$NH_2OH.HCl$<br>$NH_4$-oxalate buffer<br>$H_2O_2$<br>Acid digest. | Exchangeable metals<br>Mn oxides<br>Fe oxides<br>Organic bound metals<br>Residual fraction | Estuar. sediment<br>(Mn, Cu, Zn, Cd, Fe, Pb) | I / 384 |
| EDTA | Removal of phosphoryl-carboxyl-, sulphhydryl and hydroxyl-groups of membrane protein | Cell wall struct. components in sewage sludge (Zn, Pb, Cr) | I / 475 |
| 0.1M $CaCl_2$<br>DTPA | Correlation between bio-availability and plant uptake | Sewage sludge-soil<br>(Zn, Cu, Ni) | I / 484 |
| $H_2O$<br>$NH_4Ac$<br>Dithionite-citrate-bicarbonate buffer<br>$HCl/HNO_3$ | Water soluble<br>Exchangeable<br>Red. Fe phases<br><br>Insoluble fraction | Estuar. salt marsh sediment<br>(Fe, Mn, Zn, Cu, Cd, Pb) | I / 545 |
| 1M $KNO_3$<br>0.5M KF<br>0.1M $Na_4P_2O_7$<br>0.1M $Na_2EDTA$<br>6M $HNO_3$ | Exchangeable metals<br>Sorbed metals<br>Org. bound metals<br>Carbonate bound metals<br>Sulphides | Sewage sludge<br>(Cd, Cu, Zn, Ni, Pb) | I / 582 |

**Table 3.4.5 (cont.)**

| | | | |
|---|---|---|---|
| HAc | Leachability/immobilisation of Zn, Cu and Pb | Synthetic wastes<br>Silicate sources of cement, silicate fly ash | I / 585 |
| As in I / 384 | T1 | Soils | II / 286 |
| 1M $NH_4Ac$, pH7<br>acid digestion | Exchangeable metals<br>Total metal conc. | Soil samples<br>(Mn, Cu, Fe, Pb, Ni, Zn, Cd, Co, Ba, Mg, Ca) | II / 334 |
| 1M $MgCl_2$, pH7<br>$NH_2OH.HCl$<br>$H_2O_2/HNO_3$<br>$HF/HClO_4$ | Sorbed phase<br>Metallic coatings<br>Organic bound phase<br>Crystalline phase | Sewage sludge<br>(Cu, Cr, Zn) | II / 350 |
| Centrifugation<br>1M $NH_4Ac$ | Pore water dissolved phase<br>Exchangeable metals | Maine sediment<br>(Cd, Ag) | II / 363 |
| 0.5N HCl | Easily extractable phase (bioavailable) | Coastal susp.m. and sediment | II / 363 |

include Coggins *et al.*(1979) and Förstner *et al.*(1979). It is interesting that in the 1985 Athens Heavy Metal Conference (Reuther 1987), out of the five major extraction schemes, three are related to the schemes of Tessier *et al.*(1979) (ref. II/350), Förstner (1982) (ref. I/384) and Stover *et al.*(1976)(ref. I/582) (see Table 3.4.5 -after Reuther 1987).

## 3.5. Problems and Pitfalls of Chemical Extraction of Heavy Metals

It is a fact that chemical extraction techniques face a number of different problems. This has perhaps been highlighted by the discussion on the extraction technique of Tessier *et al.*(1979a, 1979b) by Kheboian and Bauer (1987), Tessier and Campbell (1988), Bauer and Kheboian (1988) and Belzile *et al.*(1989). Förstner (1985) reviewed a number of the problems that the technique experiences (adapted after Förstner 1985):

(a) Transformation of labile metal phases e.g. due to sample preparation (e.g. Shuman 1989), especially samples from reducing environments (e.g. Carignan 1984, Hesslein 1976).
(b) Processes of readsorption and precipitation during extraction stages (e.g. Rendell *et al.*1980, Tipping *et al.*1985).
(c) Reactions are influenced by the ratio of solid matter to volume of extractant and by the duration of the experiment. Some extractants are more specific than others. Also, too high a solid content, together with an increased buffer capacity may cause the system to overload.
(d) There are objections to the use of barium chloride / triethanolamine (TEA used to raise the pH to 8.1) or magnesium chloride for the determination of exchangeable heavy metals; there are chelating effects of TEA (an organic agent) and the formation of soluble metal-chloro-complexes. Neutral ammonium acetate seems to offer an acceptable compromise (Salomons and Förstner 1980), but this extractant is also associated with readsorption and precipitation of trace metals (Förstner 1987). This latter extractant can also attack the carbonate phase (Morrison 1987).
(e) Precipitation of metals can occur during initial high pH conditions e.g. humic extraction with sodium hydroxide or sodium pyrophosphate.
(f) The removal of carbonate phase metals has associated problems: reprecipitation under oxygenated conditions following $CO_2$ treatment; adsorption of organic compounds on exchanger resins; pH

effects on labile oxyhydrates using pH5 NaOAc/HOAc buffer. This step, though, does help to reduce the buffer capacity of the sample before applying the next leaching extraction stages (Solomons and Förstner 1980).

(g) Acid reducing stages also have problems: e.g. dithionite-citrate extraction:

(1) It is highly contaminated with metals and its purification proves difficult.
(2) The burner clogs during atomic absorption analysis because of the high salt content.
(3) Sulphide is formed as a result of the disproportionation of dithionite (formation of insoluble metal sulphides) (Förstner *et al.* 1981).

(h) Organic extracts have some of the following problems:

(1) Treatment with hydrogen peroxide affects both labile as well as relatively stable bound metal complexes - also metals released by peroxide oxidation are readily adsorbed on clays.
(2) Use of NaOH in removal of humics and fulvics can also remobilise metals from phosphates and silicates.
(3) Strong oxidising agents such as sodium pyrophosphate can also attack the crystalline phase (mainly after Morrison 1987).

(i) Treatment with organic solvents is poorly suited to routine application (Salomons and Förstner 1980).
(j) Differentiation of organic and sulphide metal associations is not clear.

Extraction procedures are not precise in their differentiation between different solid phase metal species and are not as selective as sometimes stated. Much evidence exists to suggest that sequential extractions do not cleanly remove 100% of metal in a given association (Harrison 1987). It is therefore generally accepted that partitioning of trace elements by chemical extractants is "operationally defined" (Belzile *et al.*1989) - so far as to say that experimental factors as much as the speciation of the metal in the sample are causal in the determination of the metal fraction obtained. However, despite the drawbacks of the technique, the qualitative outcome of the method provides a sensible insight into the physico-chemical factors that affect the mobility and

bioavailability of trace metals and gives confidence in the methodology (Belzile *et al.*1989, Harrison 1987, Tessier and Campbell 1987).

## 3.6. The Chemical Extraction Procedure: Hallen Wood and Haw Wood Soils

### 3.6.1. The Extraction Sequence and Extractants

A sequential extraction procedure was used to determine the heavy metal fraction-forms available in Hallen and Haw Wood soils. The sequence proposed by Coughtrey (1978) follows a similar line to the first half of the chemical extraction sequence developed by McLaren and Crawford (1973). The chemical extraction procedure follows the order:

| Extractant | Metal Fraction Extracted | | Abbreviation used in text |
|---|---|---|---|
| 1. $H_2O$ (deionised) | Water soluble | WA | "Available" |
| 2. 0.1M $NH_4NO_3$ | Easily exchangeable | AN | metals |
| 3. 0.1M $CaCl_2$ | Exchangeable and lightly bound | CC | Non-residual |
| 4. 2.5% HOAc | Strongly bound (specifically adsorbed) | AA | NRES |
| 5. 0.2M NaOH | Organically bound | SH | |
| 6. $HNO_3$ (conc.) digestion | WA+AN+CC+AA+SH Residual | RES | |

The extracted fractions are all referred to in shorthand for the rest of the chapter as WA, AN, CC, AA and SH and collectively form the non-residual fraction (i.e. WA + AN + CC + AA + SH) referred to as NRES. Subtracting the sum of the NRES fractions from the nitric acid digest total metal concentrations in the soil gives the residual fraction, referred to as RES. The total metal concentration in the soil is referred to as MTOT and is the sum of RES + NRES for that metal.

The above sequence has been used by Martin *et al.*(1976) and Coughtrey (1978). The first five steps of the extraction sequence precludes the removal of metals incorporated on and within manganese and iron oxides, residual organic matter and within lattice structures of clays. In fact, the above sequence is mainly associated with the extraction of the more mobile and/or bioavailable forms of heavy metals in the soil.

All the above extractants have been widely used for heavy metal extraction: ammonium nitrate e.g. Alloway *et al.*(1990), Davies (1983a), Davies *et al.*(1987); calcium chloride e.g. Alloway *et al.*(1990), Brümmer (1986), Jarvis and Jones (1980), McLaren and Crawford (1973), Mathur and Levesque (1988), Eriksson (1989), Zhan (1986); acetic acid e.g. Alloway *et al.* (1990), Archer and Hodgson (1987), Berrow and Mitchell (1980), Jarvis (1977), Jarvis and Jones (1980), Mathur and Levesque (1988), Mitchell (1964), Stevenson (1979), McLaren and Crawford (1973); sodium hydroxide e.g. Brümmer (1986), Chang *et al.*(1984), Emmerich *et al.*(1982a), Miller *et al.* (1986), Petruzzelli *et al.*(1981b), Sims and Patrick (1978), Sposito *et al.*(1982, 1983).

Extraction steps 1-4 can be seen to follow an order of increasing aggressivity. 0.1M $NH_4NO_3$ is not as efficient as 0.1M $CaCl_2$, but has been used in the past to extract "ecologically" exchangeable metals that are available to plants (Pigott 1958). 0.1M $CaCl_2$ should remove the remaining exchangeable metals including some that are more specifically adsorbed. The reason for using these two neutral salts for extracting exchangeable heavy metals rather than 1M $NH_4OAc$, pH7 is because the neutral salts reflect the effect of soil pH far better than the latter buffer extractant. In this respect, by not over-riding the conditions of soil pH, a more realistic measure of exchangeable metals available for mobility and plant uptake in the soil is achieved. A comparison of cadmium extracted by 1M $NH_4OAc$ and 0.05M $CaCl_2$ was made by Eriksson (1989) in clay and sand soil where the effect of soil pH was most clearly demonstrated upon the use of the calcium chloride extractant - especially in the clay soil (see Fig.3.6.1). It is important to take this factor into account because of the important effect that pH has on the solubility / availability of heavy metals in soils.

The 2.5% acetic acid is a more aggressive extractant than the two neutral salts, and with an acidity of about pH2.5, is able to remove those metals that are strongly bound (specifically adsorbed). These may include many heavy metals that are precipitated (e g. to carbonates) and some metals that are co-precipitated with amorphous hydrous oxides. Dilute acetic acid is a useful extractant in assessing "available" heavy metals for plant uptake and is more often used than ammonium acetate, pH7 (Jarvis 1977, Jones and Jarvis 1981). Step 5 of the extraction sequence uses 0.2M sodium hydroxide, the employment of which is used more specifically to remove heavy metals bound to humic substances. This alkali soluble fraction may also remove a small amount of metals from inorganic sites e.g. amorphous hydrous oxides (Pickering 1981).

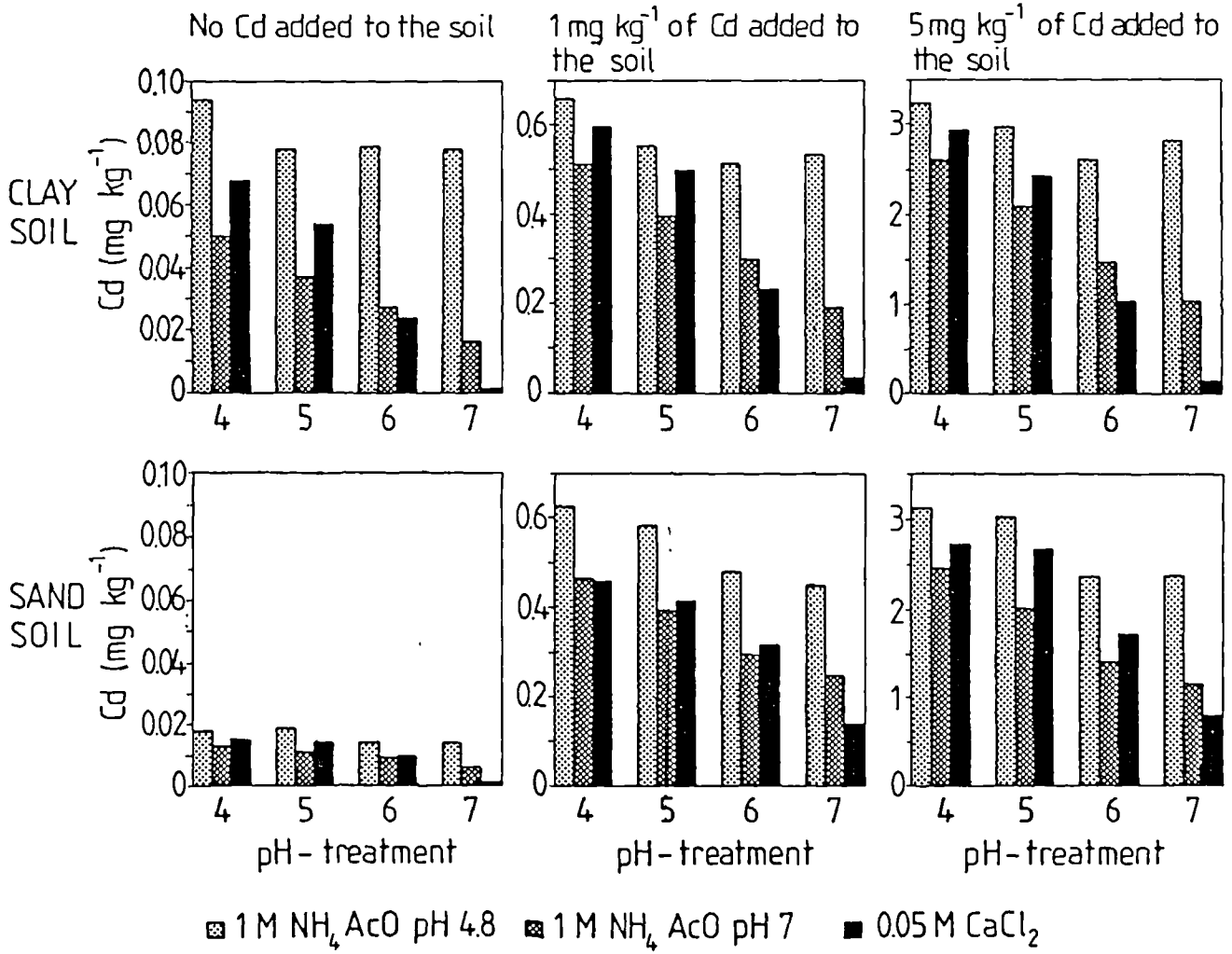


Fig.3.6.1 Average amounts of soil Cd extractable in 1 M $NH_4AcO$ pH 4.8 (ama4.8), 1 M $NH_4AcO$ pH 7 (ama7) and 0.05 M $CaCl_2$ for different pH-treatments, Cd-treatments and soil types. Data are from sampling 2 in year 2 (n=2).

**Table 3.6.1 % Efficiency of Acid Digests in the Extraction of Lead from Soils in Relation to X-Ray Fluorescence Measurement (after Eastwood and Jackson 1984).**

Number of laboratories (n) using digestion technique

| | $HNO_3$ * | $HNO_3$ ‡ | $HNO_3$/ HCl * | $HNO_3$/ $HClO_4$ * |
|---|---|---|---|---|
| | n = 10 | n = 2 | n = 3 | n = 5 |
| Soil A (sandy loam) | 89 ± 8 | 88 ± 8 | 84 ± 5 | 94 ± 18 |
| Soil B (coarse loam) | 85 ± 16 | 104 | 91 ± 12 | 68 ± 16 |
| Soil C (silty loam) | 104 ± 8 | 97 | 101 ± 7 | 112 ± 10 |

* : FAAS - Flame Atomic Absorption Spectrophotometry
‡ : ET-AAS - Electro-Thermal Atomic Absorption Spectrophotometry

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Concentrated nitric acid is used to obtain the total metal concentrations in the soil. The relative efficiency of the concentrated $HNO_3$ has been assessed by several authors in aquatic, estuarine and marine sediment metal extractions. Although boiling concentrated nitric acid may compare less favourably with techniques such as X-ray fluorescence (Hall and Chang-Yen 1989) or HF-$HNO_3$-$HClO_4$ acid mix (PTFE bomb) digest (Agemian and Chau 1976) for the assessment of total heavy metals in sediments, it does, however, compare very favourably with other commonly used acid digestion techniques such as aqua regia, nitric-perchloric acid mix (Agemian and Chau 1976) and hydrofluoric acid (Luoma and Bryan 1981). Concentrated nitric acid alone (e.g. at 100°C for one hour) is an efficient method for the determination of Cu, Pb, Zn and Cd in soils and sediments (Thompson 1983). In an inter-laboratory comparison of soil lead determinations from 22 laboratories on three different soil types, it was found that for digesting the soils, nitric, nitric / hydrochloric, and nitric / perchloric acids were equally effective (Eastwood and Jackson 1984). Table 3.6.1 summarises the results from this study. The amount of metal in RES of the extraction procedure also accounts for metals that might be obtained by vigorous disruptive reagents such as ammonium oxalate or acidified hydrogen peroxide; but these are the more immobile forms of heavy metals in the soil (Berrow and Mitchell 1980).

## 3.6.2. Materials and Methods

20 grams of air-dried soil (<2mm in size) were weighed into polyurethane bottles to which 50mls of extractant were added. Samples were then shaken for one hour before filtering through Whatman No.50 filters. After filtering, leachate samples were preserved in 20% nitric acid. The soil residue from this extraction was then reused for the next stage of the sequential extraction. Each sample was carried out in triplicate.

Air-drying of soil is a departure from the natural state of the soil in the field. The problems of sample preparation in sediments (Rapin *et al.*1986) and soils (Shuman 1980) have been identified; but the use of dried soil (<2mm in size) is recognised as the standard preparative technique for soil analysis of heavy metals, and air-dried soil is usually employed for the sequential extraction of heavy metals.

Prepared sample solutions were analysed by flame atomic absorption spectrophotometry (see Appendix A). Negligible or no chemical interferences were recorded for WA, AN, AA and SH for all four heavy metals. Cu and Zn suffered no interference from CC, but Pb and Cd suffered a small amount of translational bias that was taken into account. This interference was probably a result of the high concentration of Ca ions in solution. Such bias for Pb and Cd caused by Ca has been reported by Thompson (1983).

## 3.6.3. Sequential Extraction Results for Haw Wood

The results have been summarised in Figs.3.6.2 and 3.6.3. Fig.3.6.2 illustrates the total cumulative concentration of each metal extracted (i.e. $\Sigma$ WA + AN + CC + AA + SH) in relation to the total soil metal metal concentrations, MTOT (i.e. $\Sigma$ WA + AN + CC + AA + SH + RES). The most obvious feature of Fig.3.6.2 is the portrayal of a system dominated by the RES fraction more than any other fraction. This was particularly true of Pb and Cu, where 98% or more of the metals were in a RES form. However, Zn and Cd were more available in NRES forms. 8-13% of the Zn was NRES in the top 11cm of soil, whereas 20% of the Cd was NRES throughout the entire profile (despite NRES Cd concentrations decreasing to <0.5 mg/kg at depths >10cm). The availability of the metals (NRES) in relation to MTOT therefore followed the order:

$$Cd > Zn > Cu = Pb$$

Despite the larger concentrations of metals sequentially extracted from the L, F and H layers, these proportionally represented a much smaller fraction of NRES metals than was obtained in the top 11cm of mineral soil. This was perhaps related to the relative affinity that organic matter has for binding heavy metals and/or due to the relatively inert form of metal deposition upon the litter surface.

Fig.3.6.3 further expounds the data by omitting the RES data. NRES Cd, Zn and Pb concentrations tended to reflect their MTOT ($r = 0.999$, $r = 0.995$, $r = 0.765$ respectively); Cu was anomalous in this respect ($r = 0.041$). The AA fraction was the dominant NRES fraction for Cd, Zn and Pb. The AA fraction was also important for Cu, but was far more subordinate in relation to SH as soil depth decreased.

### (A) Correlation of Easily Exchangeable Heavy Metals with Various Soil Variables

The easily exchangeable (EXCH) heavy metals ($\Sigma$ WA + AN) have been correlated against other soil variables including EXCH metals (Na, K, Mg, Ca, Al, Mn, Fe, Cd, Zn, Pb, Cu), NRES metals (Fe, Mn, Cd, Zn, Pb, Cu), MTOT metals (K, Ca, Al, Mn, Fe, Cd, Zn, Cu, Pb) and seven principal soil environmental variables (depth, % carbon [%C], bulk density, pH, total exchangeable hydrogen [$\Sigma H^+$], cation-exchange-capacity [C.E.C.], and

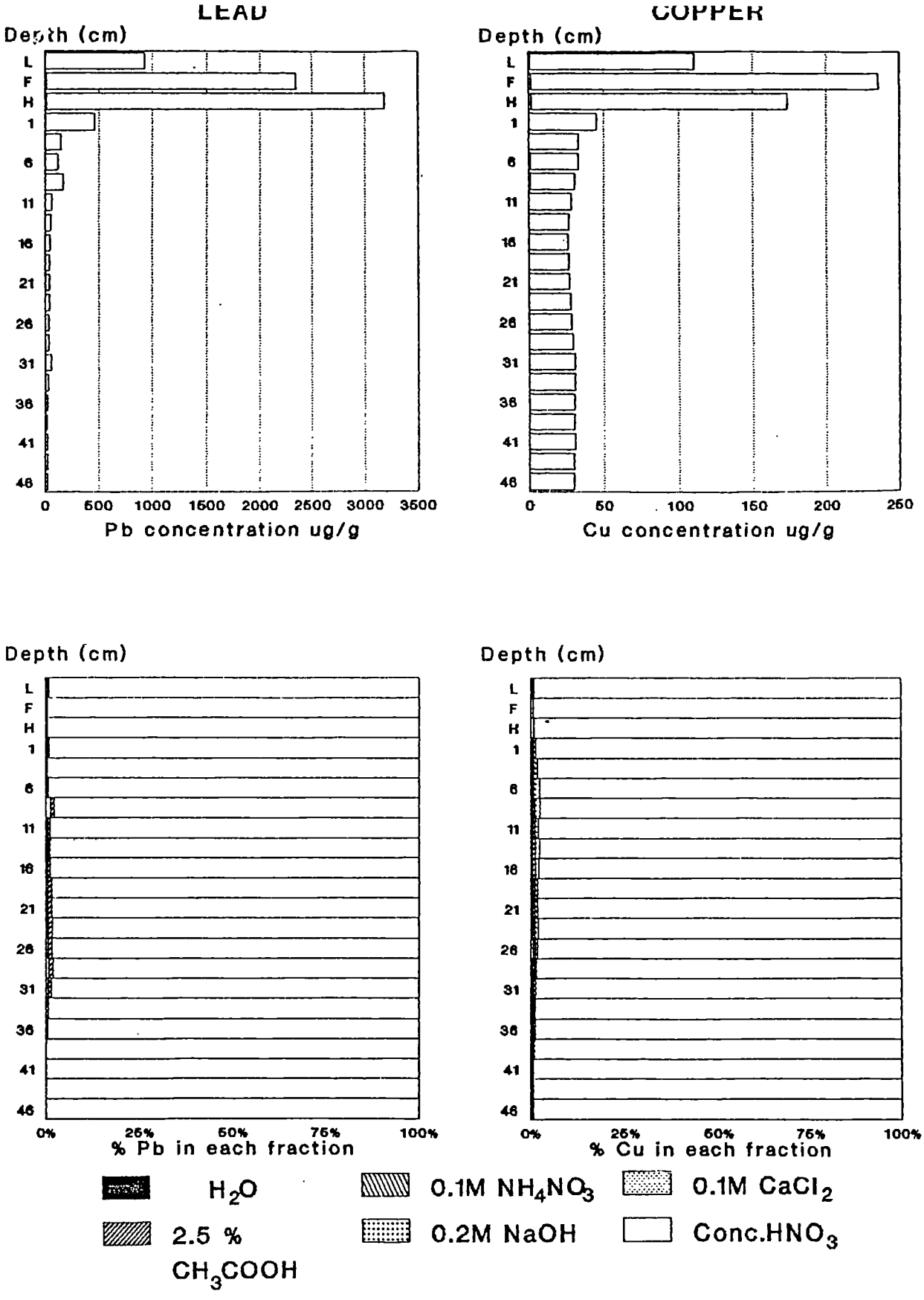


Fig.3.6.2a Pb and Cu data for the sequential extraction of Haw Wood soil profile (1987). These data include the residual ($HNO_3$) extract. The histogram bars are cumulative concentrations and percentages. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

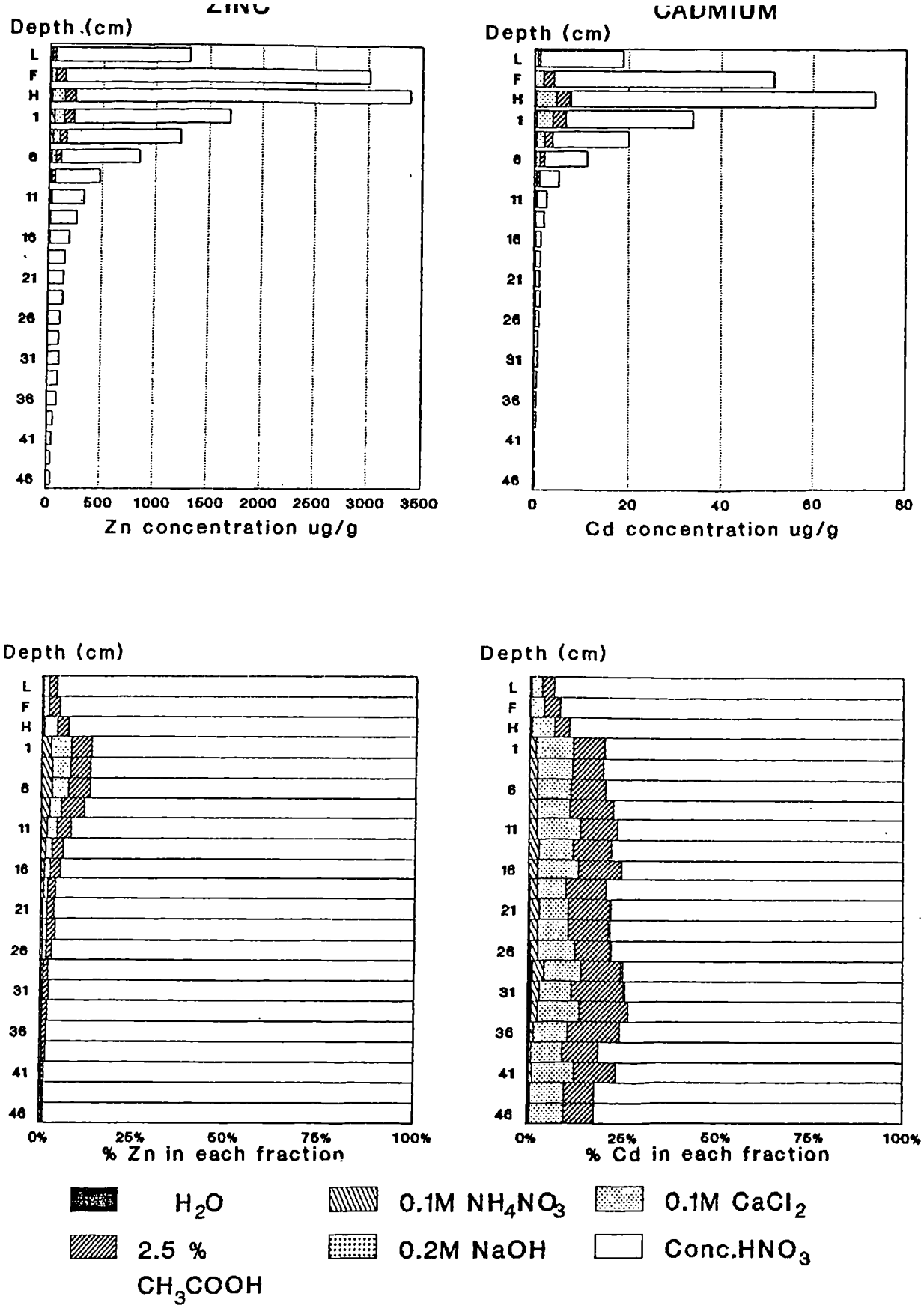


Fig.3.6.2b Zn and Cd data for the sequential extraction of Haw Wood soil profile (1987). These data include the residual ($HNO_3$) extract. The histogram bars are cumulative concentrations and percentages. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

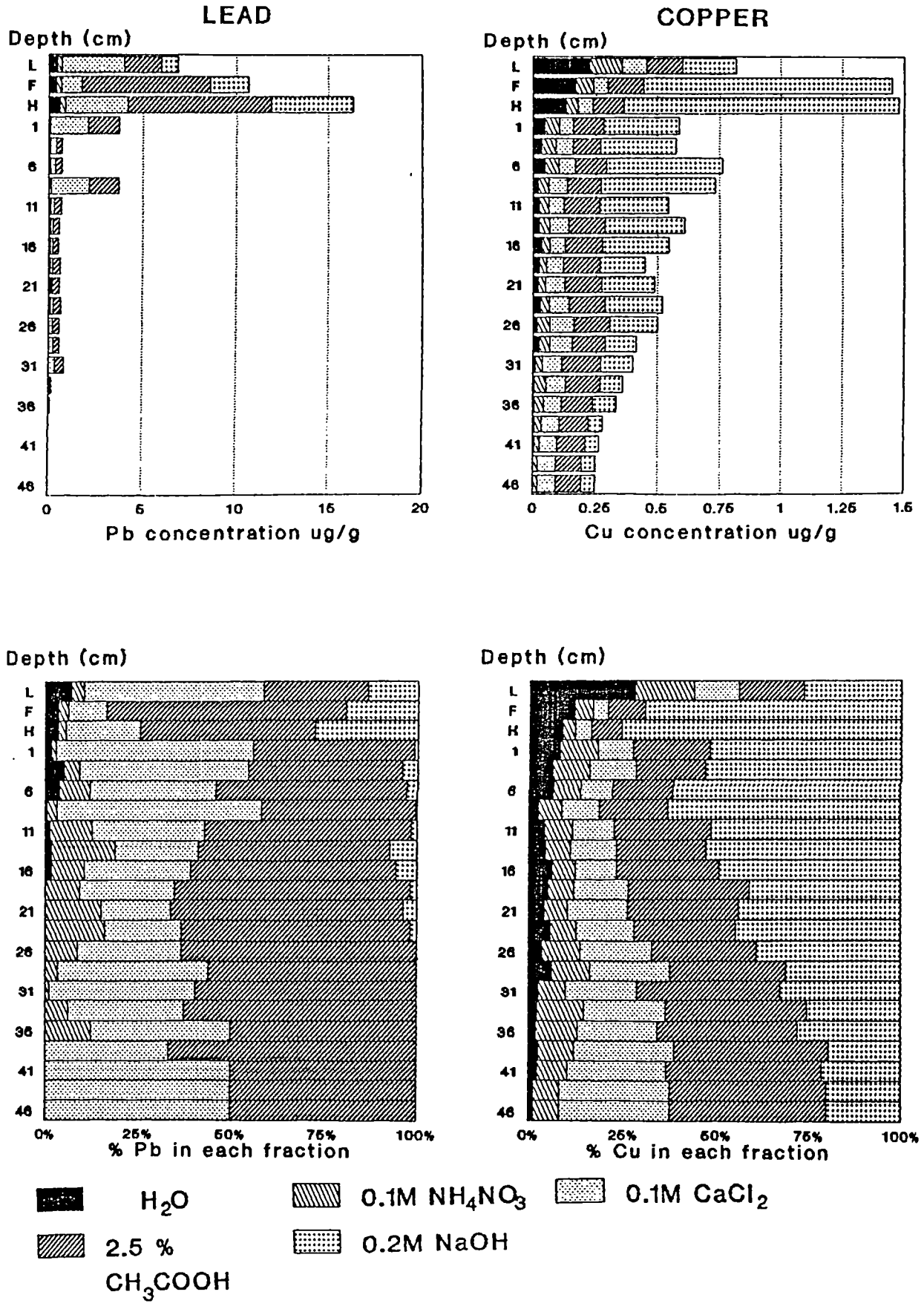


Fig.3.6.3a Pb and Cu data as in Fig.3.6.2a but omitting residual ($HNO_3$) extraction. The histogram bars are for cumulative concentrations. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

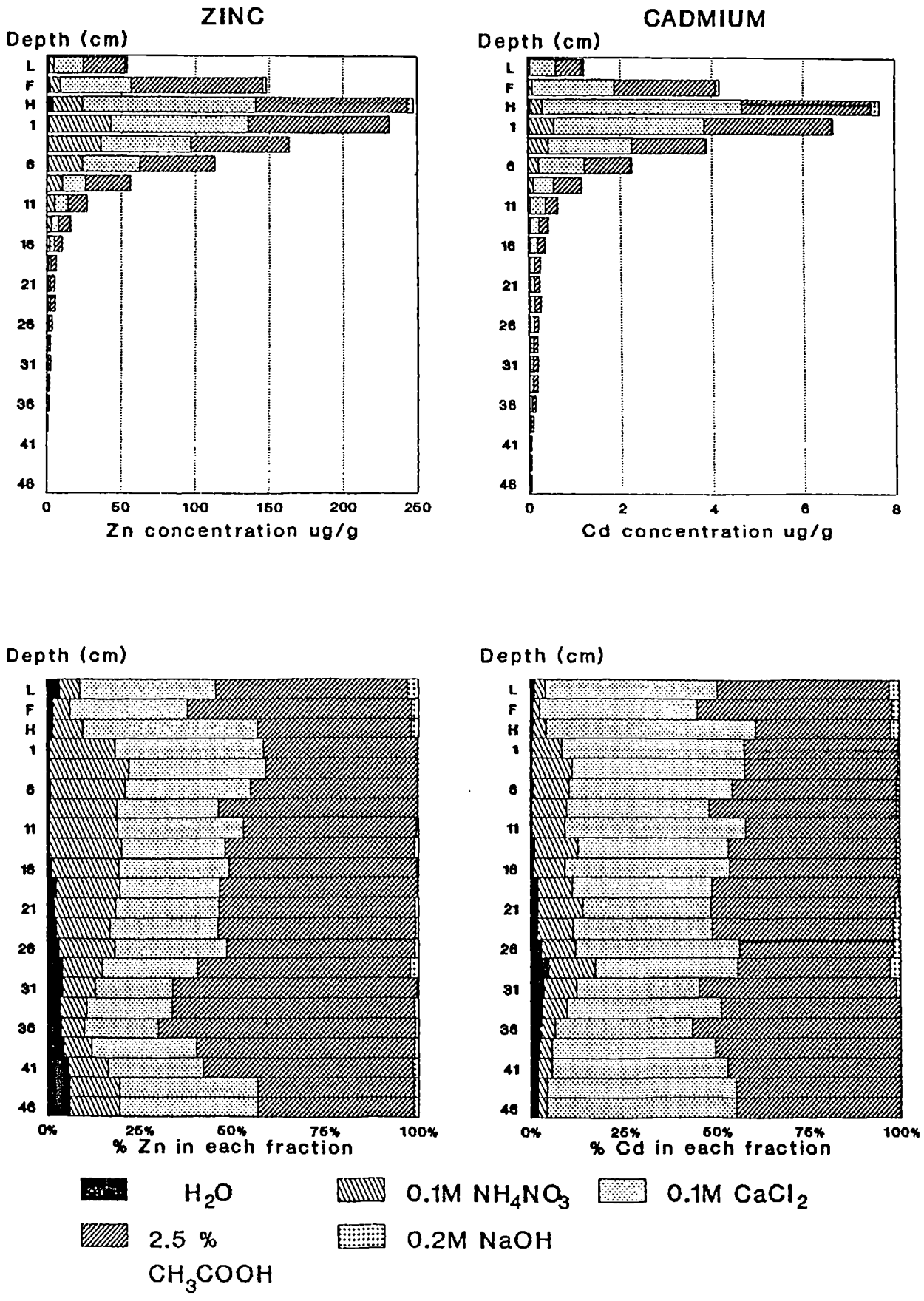


Fig.3.6.3b Zn and Cd data as in Fig.3.6.2b but omitting residual ($HNO_3$) extraction. The histogram bars are for cumulative concentrations. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

% base saturation [%B.S.]). The L, F, H and 0-1cm layers have been discounted so that excessively high / low values are excluded which might have a significant effect on the outcome of the correlation value. The Pearson's product moment correlation coefficient (r) was calculated, where n = 17. Correlation coefficients at or >±0.800 were considered so that a significance level of much <0.1% was achieved. The results are shown in Table 3.6.2.

The fact that both Cd and Zn are known to be geochemically similar to each other is demonstrated by the fact that EXCH Cd and Zn clearly were inextricably related to each other within the soil profile. MTOT Cd / Zn, NRES Cd / Zn and EXCH Cd / Zn are very highly correlated to each other indicating how close the geochemical ties were between these two metals in this particular soil system. MTOT Pb also had a reasonably high positive coefficient with EXCH Cd and Zn, and this perhaps reflected the high level of aerial input of these three metals into the Haw litter and topsoil in relation to their background concentrations. EXCH K and %C both shared reasonably high correlation coefficients with EXCH Cd and Zn. EXCH K was closely linked with %C (r = 0.979), and it would appear that %C (organic matter) distribution was affiliated to the distribution of EXCH Cd, Zn and K in the mineral soil profile.

EXCH Cu was highly correlated to EXCH K, bulk density and %C. These variables were also highly correlated with each other (r => ±0.950). MTOT Ca, depth and C.E.C. were also highly related to %C (r => ±0.900). It would appear that organic matter (%C/bulk density) was also important in explaining the EXCH Cu distribution, although the discrepancy between organic matter and depth was not as clear as it was for Cd and Zn. However, EXCH Pb related to variables such as NRES Cu, EXCH Mn, EXCH Mg, C.E.C. and depth. These variables were all highly depth related (r => ±0.930). Depth would appear to be the most important variable correlating with EXCH Pb.

## (B) Correlation of Non-Residual Heavy Metals with Various Soil Variables

The same conditions and soil variables mentioned in Section 3.6.3(A) apply also to this section. The results are shown in Table 3.6.3.

NRES Cd and Zn both highly correlated with their respective EXCH metals (r = 0.998 and r = 0.999 respectively) and hence, as explained in Section 3.6.3(A), organic matter (%C) would appear to be the principal environmental factor that correlated best with their distributions in the Haw soil profile.

**Table 3.6.2 Statistically significant (p<0.1%) correlation coefficients between exchangeable (EXCH) Cd, Cu, Pb, Zn and numerous soil variables. (Haw Wood)**

| Independent Significant x Variables | | y Dependent Variables: Exch. Cd | Exch. Zn | Exch. Cu | Exch. Pb |
|---|---|---|---|---|---|
| Total soil | Cd | 0.998 | 0.995 | - | - |
| | Zn | 0.986 | 0.994 | - | - |
| | Pb | 0.797 | 0.821 | - | - |
| | Ca | - | - | 0.858 | - |
| Total | Cd | 0.998 | 0.996 | - | - |
| Extractable | Zn | 0.986 | 0.999 | - | - |
| | Cu | - | - | 0.851 | 0.877 |
| | Mn | - | - | - | 0.838 |
| Exchangeable | Cd | - | 0.990 | - | - |
| | Zn | 0.990 | - | - | - |
| | K | 0.876 | 0.889 | 0.892 | - |
| | Mg | - | - | 0.800 | 0.838 |
| | Mn | - | - | - | 0.902 |
| Anionic | $Cl^-$ | 0.721 | 0.765 | - | - |
| | $NO_3^-$ | 0.908 | 0.925 | - | - |
| Depth | | - | - | -0.856 | -0.844 |
| pH | | - | - | - | - |
| % Carbon | | 0.844 | 0.862 | 0.884 | - |
| Bulk Density | | - | - | -0.897 | - |
| Exchangeable $H^+$ | | - | - | 0.864 | - |
| Cation-Exchange-Capacity | | - | - | 0.874 | 0.797 |
| % Base Saturation | | - | - | - | - |

n = 17 p =< 0.1%

**Table 3.6.3 Statistically significant (p<0.1%) correlation coefficients between total extractable (NRES) Cd, Cu, Pb, Zn and numerous soil variables. (Haw Wood)**

| Independent Significant x Variables | | y Dependent Variables: Total Extr. Cd | Total Extr. Zn | Total Extr. Cu | Total Extr. Pb |
|---|---|---|---|---|---|
| Total soil | Cd | 0.999 | 0.991 | - | - |
| | Zn | 0.992 | 0.995 | - | - |
| | Pb | 0.817 | 0.842 | - | - |
| | Ca | - | - | 0.878 | - |
| Total Extractable | Cd | - | 0.994 | - | - |
| | Zn | 0.994 | - | - | - |
| | Mn | - | - | 0.866 | - |
| Exchangeable | Cd | 0.998 | 0.986 | - | - |
| | Zn | 0.996 | 0.999 | - | - |
| | Cu | - | - | 0.851 | - |
| | K | 0.885 | 0.900 | 0.871 | - |
| | Mg | - | - | 0.907 | - |
| | Mn | - | - | 0.934 | - |
| | Pb | - | - | 0.877 | - |
| Anionic | $Cl^-$ | 0.749 | 0.790 | 0.791 | 0.784 |
| | $NO_3^-$ | 0.920 | 0.924 | - | - |
| Depth | | - | - | -0.929 | - |
| pH | | - | - | - | - |
| % Carbon | | 0.857 | 0.877 | 0.905 | - |
| Bulk Density | | -0.791 | -0.808 | -0.938 | - |
| Exchangeable $H^+$ | | - | - | 0.817 | - |
| Cation-Exchange-Capacity | | - | - | 0.866 | - |
| % Base Saturation | | - | - | - | - |

**Table 3.6.4 Multiple Relationships between Exchangeable and Total Extractable Cd, Zn, Cu and Pb concs. (mg/kg) of Haw Wood Soils and certain Soil Variables, according to Stepwise Regression Analysis**

"Independant" variables : Depth, pH, % Carbon, Exchangeable $H^+$, Cation-Exchange-Capacity (C.E.C.) and % Base Saturation (%B.S.)

| | Exchangeable | | | Total Extractable | | |
|---|---|---|---|---|---|---|
| | Step no. Variables Entered | Multiple $100r^2$ | Simple r | Step no. Variables Entered | Multiple $100r^2$ | Simple r |
| Cd | 1. % Carbon | 71.23 | 0.844 | 1. % Carbon | 73.53 | 0.857 |
| | 2. Depth | 83.49 | -0.693 | 2. Depth | 86.66 | -0.702 |
| | 3. C.E.C. | 87.74 | 0.705 | | | |
| Zn | 1. % Carbon | 74.39 | 0.862 | 1. % Carbon | 76.96 | 0.877 |
| | 2. Depth | 89.90 | -0.697 | 2. Depth | 91.91 | -0.713 |
| Cu | 1. % Carbon | 78.15 | 0.884 | 1. Depth | 86.34 | -0.929 |
| | 2. % B.S. | 84.70 | -0.750 | | | |
| Pb | 1. Depth | 71.24 | -0.844 | 1. % Carbon | 29.93 | 0.547 |

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However, (unlike Cd and Zn) NRES Cu was not as highly correlated with EXCH Cu ($r = 0.851$). Therefore, whereas for EXCH Cu, organic matter related variables (%C, bulk density) tended to correlate highest (see Section 3.6.3[A]), for NRES Cu, depth related variables were also equally important (e.g. EXCH Mg and Mn, and depth with $r => 0.900$). NRES Pb had no correlations with any other variable at or greater than $\pm 0.800$. The only significant correlation at the 0.1% level was with MTOT Pb ($r = 0.765$).

## (C) Stepwise Multiple Regression of Easily Exchangeable / Non-Residual Heavy Metals on Six Principal Soil Environmental Variables

Six principal soil variables have been considered in order to explain the variation in the distribution of EXCH and NRES heavy metals in the soil at Haw Wood. The results are given in Table 3.6.4.

The most striking feature of Table 3.6.4 would appear to be the importance of % C and depth in explaining the distribution of EXCH and NRES heavy metals. However, %C and depth were both highly correlated (r = -0.950), a factor which would invalidate the concept of multiple regression where the two variables have been entered (multicollinearity). Nevertheless, partial correlations ($r_{123}$) indicate that when depth is excluded the correlation between % C and EXCH/NRES Cd and Zn is still well maintained, lending some support to the idea that %C was influential in the outcome of the distribution of available Cd and Zn in Haw soil:

| variables r1 | r2 | correlation r12 | variable r3 | correlation r12.3 | |
|---|---|---|---|---|---|
| EXCH Cd, | %C | 0.844 | depth | 0.810 | * |
| NRES Cd, | %C | 0.857 | depth | 0.850 | * |
| EXCH Zn, | %C | 0.862 | depth | 0.893 | * |
| NRES Zn, | %C | 0.877 | depth | 0.912 | * |
| EXCH Cu, | %C | 0.884 | depth | 0.439 | N.S |
| NRES Cu, | %C | 0.905 | depth | 0.194 | N.S |
| EXCH Pb, | %C | 0.738 | depth | 0.381 | N.S |
| NRES Pb, | %C | 0.547 | depth | 0.414 | N.S |

* = p<0.1%, N.S. = p>5%

## 3.6.4. Sequential Extraction Results for Hallen Wood

Data for Hallen Wood have been summarised (as for Haw Wood data in Section 3.6.3) in Figs.3.6.4 and 3.6.5. In Fig.3.6.4, the RES fraction predominates within the soil. It was the single most important individual extracted fraction. More than 90% of the Pb and Cu were RES. Zn and Cd had far more metal than Pb and Cu in NRES form: 20-30% for Zn in the mineral soil to 36cm depth and 50-70% for Cd to 51cm depth. Although RES Cd and Zn were the largest single extracted fractions of those metals in the soil, it is quite apparent, however, that a significant proportion of the soil profile had > 10% of Cd to 51cm depth in EXCH form. The proportion of the NRES form of the four metals in relation to their MTOT decreased in the order :

$$Cd > Zn > Cu = Pb$$

As in Haw Wood (Section 3.6.3), organic matter would appear to have been important in binding the metals in the L, F, H and 0-1cm layers as the proportion of NRES metals was much diminished in relation to the proportions

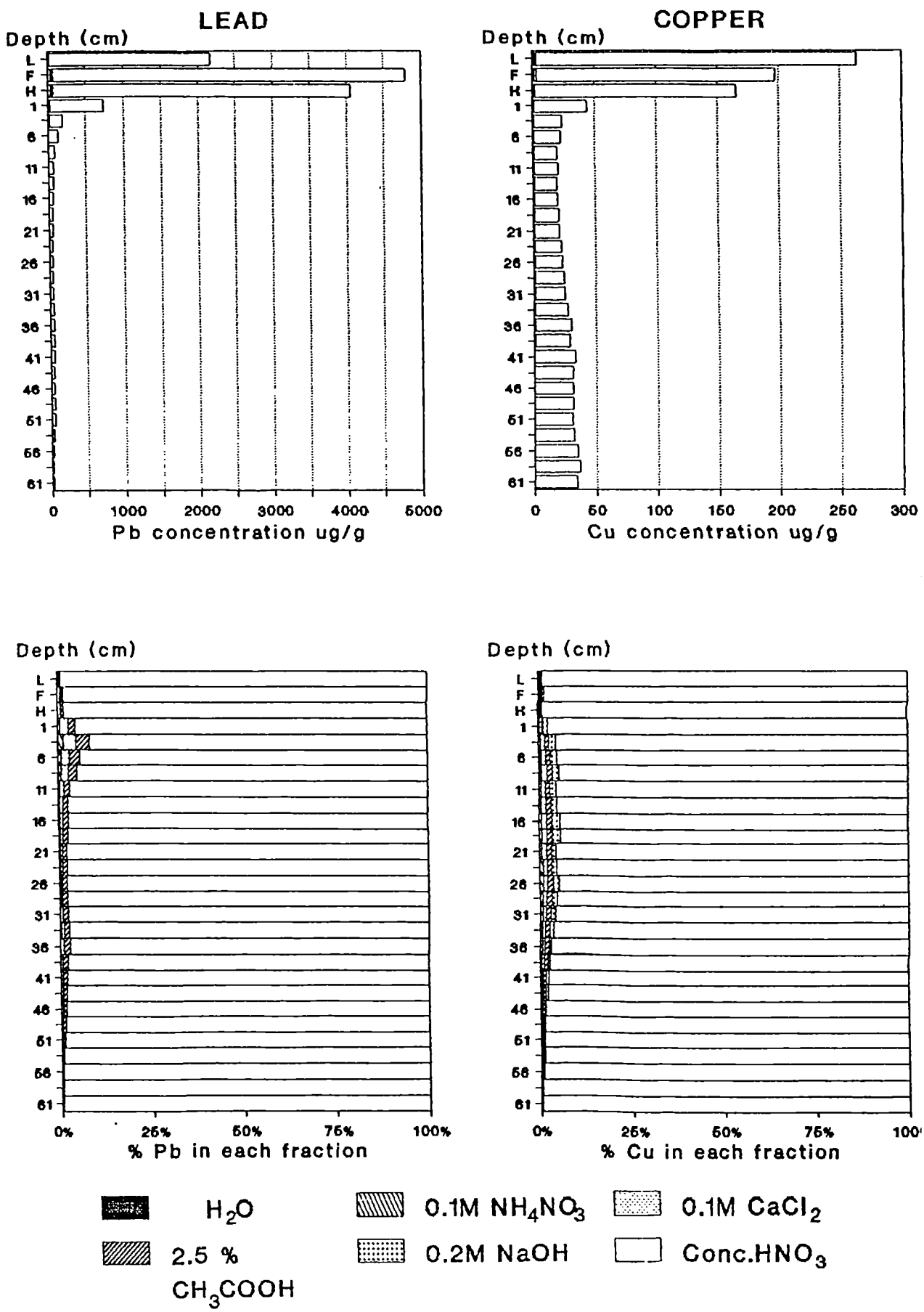


Fig.3.6.4a Pb and Cu data for the sequential extraction of Hallen Wood soil profile (1987). These data include the residual ($HNO_3$) extract. The histogram bars are cumulative concentrations and percentages. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

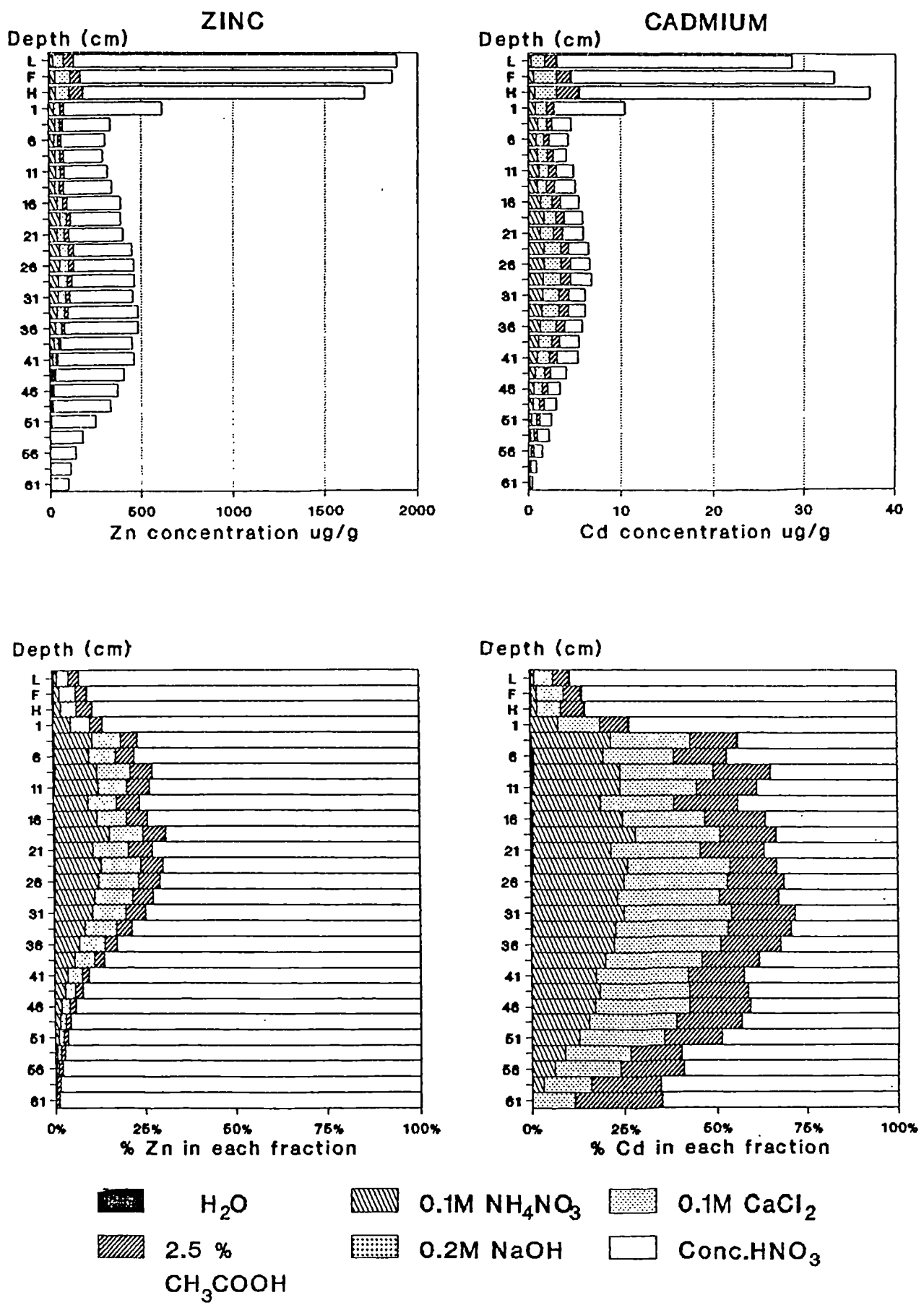


Fig.3.6.4b Zn and Cd data for the sequential extraction of Hallen Wood soil profile (1987). These data include the residual ($HNO_3$) extract. The histogram bars are cumulative concentrations and percentages. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

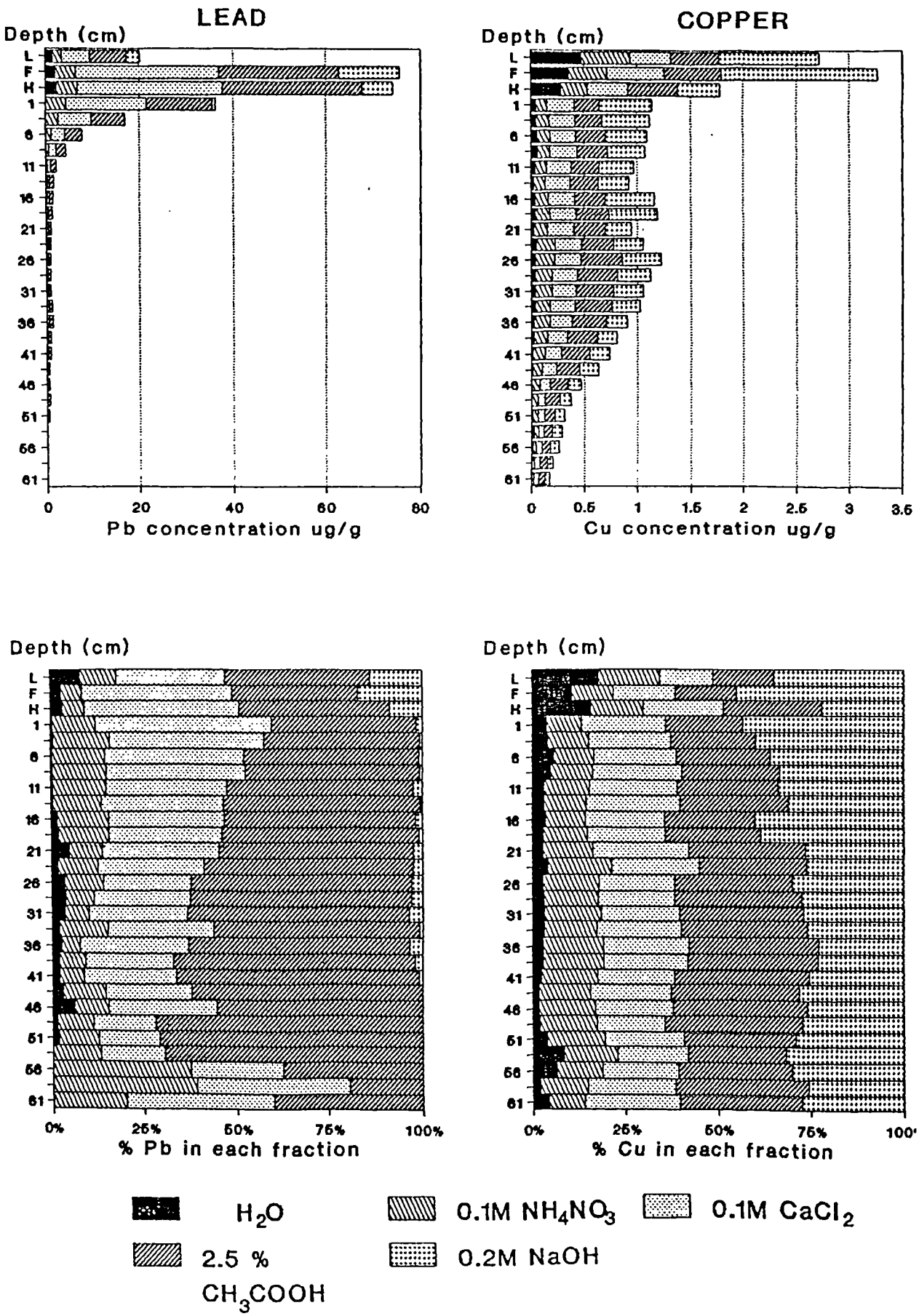


Fig.3.6.5a Pb and Cu data as in Fig.3.6.4a but omitting residual ($HNO_3$) extraction. The histogram bars are for cumulative concentrations. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

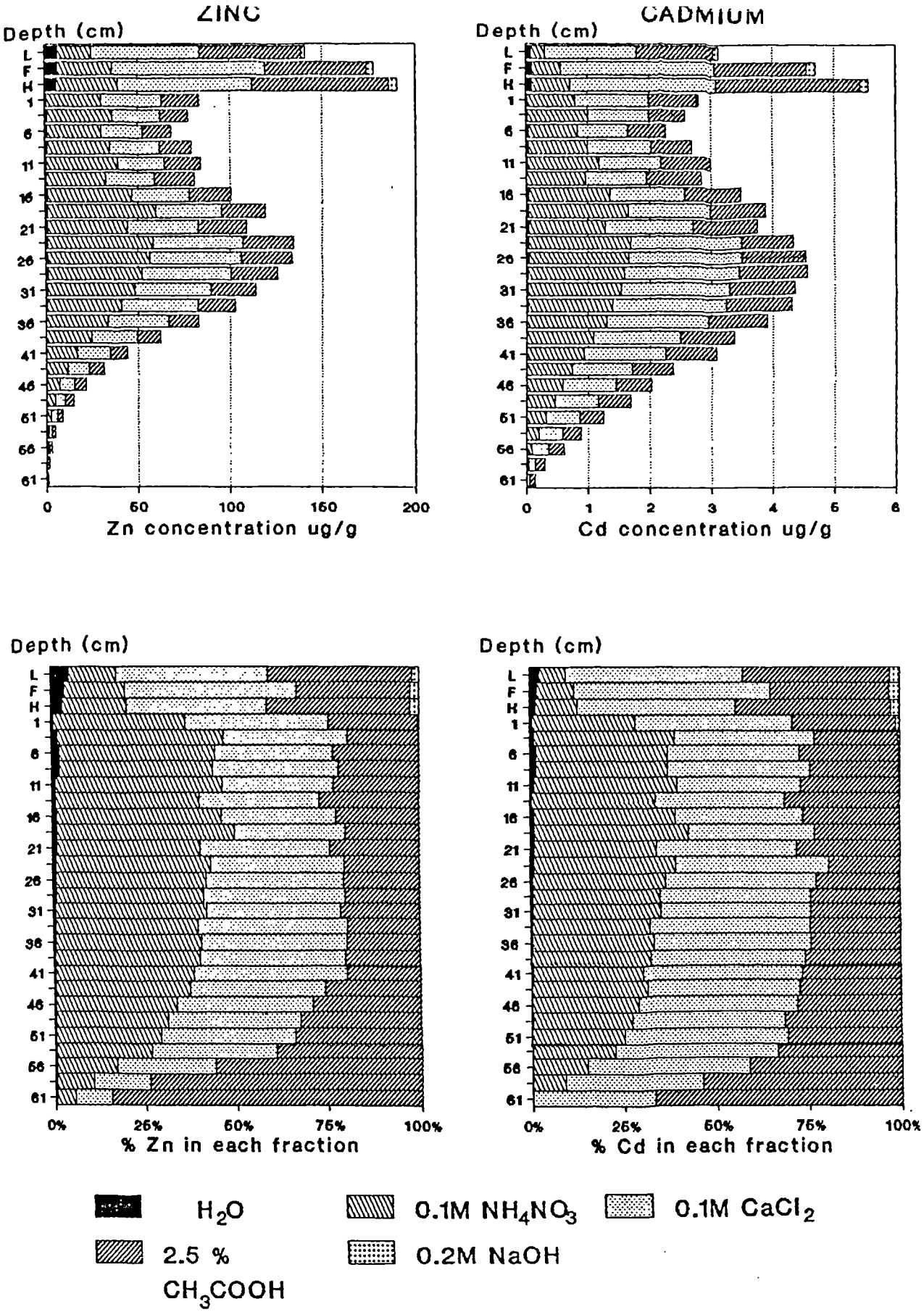


Fig.3.6.5b Zn and Cd data as in Fig.3.6.4b but omitting residual ($HNO_3$) extraction. The histogram bars are for cumulative concentrations. Top diagrams = concentration data; bottom diagrams = data expressed as percentages of total metal concentrations extracted.

extracted deeper down the Hallen profile (despite MTOT concentrations in the organic layers being excessively higher than those in the mineral soil layers).

A more lucid portrayal of the sequentially extracted data is given in Fig.3.6.5. NRES Cd, Zn and Pb all tended to reflect their MTOT concentrations ($r = 0.987$, $r = 0.746$, $r = 0.972$); as in Haw Wood, Cu was the anomaly ($r = -0.859$). The AA fraction was an important fraction for Pb; and a large proportion of the geochemically more mobile metals (Cd and Zn) were hallmarked with the presence of a high proportion of EXCH metal, although an acute increase occurred in the proportion of the AA fraction at the base of the Hallen profile. The last three layers of the Pb profile in Fig.3.6.5 might suggest that proportionally, Pb had become more mobile at the base of the profile, but this is purely an artifact of the poor detection limit of Pb on FAAS (i.e. the Pb measured in these three layers was at or below the detection limit).

## (A) Correlation of Easily Exchangeable Heavy Metals with Various Soil Variables

The same conditions and soil variables mentioned in Section 3.6.3(A) apply to this section. The only difference is that $n = 24$. Also correlations of $> \pm 0.700$ were considered for the principal soil environmental variables as no correlations $> \pm 0.800$ were attained. $r = 0.700$ is significant at the 0.1% confidence limit for Hallen data (see Table 3.6.5).

EXCH Cd and Zn were (as for Haw Wood) highly correlated with each other. The close geochemical association that these two metals are known to have with each other is amplified by the very high correlation coefficients that MTOT Cd / Zn, NRES Cd / Zn and EXCH Cd / Zn all possessed. NRES and EXCH Cu were also highly correlated with the distribution of EXCH Cd / Zn. The other variable that appeared to be closely associated to EXCH Cd / Zn was EXCH K. NRES and EXCH Cu, EXCH K and NRES/EXCH Mn correlated most highly with pH related variables such as pH (EXCH K, $r = -0.818$; NRES Mn, $r = -0.857$), $\Sigma H^+$, and %B.S. (EXCH Cu, $r = -0.806$; NRES Cu, $r = -0.881$; EXCH Mn, $r = -0.900$). Depth related variables such as MTOT Ca, Cu and Fe, and EXCH Al / Na also seemed to be important in explaining the EXCH Zn distribution. The water soluble anions, $NO_3^-$ and $SO_4^{2-}$, were highly correlated with EXCH Cd, Zn and Cu, and were also closely associated with the environmental variables pH and %B.S. (see Chapter 4, Section 4 for further details). Interestingly, MTOT Mn correlated highly with EXCH Cd and Zn, but had no significant correlations with any of

**Table 3.6.5 Statistically significant (p<0.1%) correlation coefficients between exchangeable (EXCH) Cd, Cu, Pb, Zn and numerous soil variables. (Hallen Wood)**

| Independent Significant x Variables | | y Dependent Variables | | | |
|---|---|---|---|---|---|
| | | Exch. Cd | Exch. Zn | Exch. Cu | Exch. Pb |
| Total soil | Cd | 0.969 | 0.892 | 0.930 | - |
| | Zn | 0.861 | - | - | - |
| | Cu | - | -0.830 | - | - |
| | Pb | - | - | - | 0.964 |
| | Mn | 0.810 | 0.814 | - | - |
| | Fe | - | -0.812 | -0.825 | - |
| | Ca | - | -0.844 | -0.837 | - |
| Total Extractable | Cd | 0.982 | 0.907 | 0.926 | - |
| | Zn | 0.972 | 0.993 | 0.948 | - |
| | Cu | 0.925 | 0.943 | 0.959 | - |
| | Pb | - | - | - | 0.999 |
| | Mn | 0.872 | 0.858 | 0.948 | - |
| | Fe | - | - | - | 0.817 |
| Exchangeable | Cd | - | 0.963 | 0.949 | - |
| | Zn | 0.963 | - | 0.938 | - |
| | Cu | 0.949 | 0.938 | - | - |
| | Mn | 0.850 | 0.874 | 0.920 | - |
| | Al | - | 0.845 | - | - |
| | Na | -0.821 | -0.896 | -0.819 | - |
| | K | 0.975 | 0.916 | 0.945 | - |
| Anionic | $NO_3^-$ | 0.884 | 0.904 | 0.892 | - |
| | $SO_4^{2-}$ | 0.849 | 0.789 | 0.883 | - |
| Depth | | - | -0.764 | -0.772 | - |
| pH | | -0.757 | -0.725 | -0.797 | - |
| % Carbon | | - | - | 0.701 | - |
| Bulk Density | | - | - | -0.0.723 | - |
| Exchangeable $H^+$ | | 0.715 | 0.753 | 0.776 | - |
| Cation-Exchange-Capacity | | - | - | - | - |
| % Base Saturation | | -0.763 | -0.795 | -0.806 | - |

n = 24 p =< 0.1%

**Table 3.6.6 Statistically significant (p<0.1%) correlation coefficients between total extractable (NRES) Cd, Cu, Pb, Zn and numerous soil variables. (Hallen Wood)**

| Independent Significant x Variables | | y Dependent Variables: Total Extr. Cd | Total Extr. Zn | Total Extr. Cu | Total Extr. Pb |
|---|---|---|---|---|---|
| Total soil | Cd | 0.987 | 0.919 | 0.894 | - |
| | Zn | 0.924 | - | - | - |
| | Cu | - | -0.806 | -0.859 | - |
| | Pb | - | - | - | 0.972 |
| | Mn | 0.792 | 0.829 | - | - |
| | Fe | - | - | -0.897 | - |
| | Ca | - | -0.825 | -0.920 | - |
| Total Extractable | Cd | - | 0.936 | 0.880 | - |
| | Zn | 0.936 | - | 0.935 | - |
| | Cu | 0.880 | 0.935 | - | - |
| | Mn | 0.848 | 0.862 | 0.928 | - |
| | Fe | - | - | - | 0.827 |
| Exchangeable | Cd | 0.982 | 0.972 | 0.925 | - |
| | Zn | 0.907 | 0.993 | 0.943 | - |
| | Cu | 0.926 | 0.948 | 0.959 | - |
| | Pb | - | - | - | 0.999 |
| | Mn | - | 0.858 | - | - |
| | Al | - | 0.807 | 0.870 | - |
| | Na | - | -0.871 | -0.896 | - |
| | K | 0.963 | 0.922 | 0.930 | - |
| | Mg | - | - | -0.868 | - |
| Anionic | $NO_3^-$ | 0.871 | 0.930 | 0.836 | - |
| | $SO_4^{2-}$ | 0.859 | 0.809 | 0.800 | - |
| Depth | | - | -0.734 | -0.880 | - |
| pH | | -0.735 | -0.721 | -0.853 | - |
| % Carbon | | - | - | 0.727 | - |
| Bulk Density | | -0.710 | - | -0.746 | - |
| Exchangeable $H^+$ | | - | 0.734 | 0.864 | - |
| Cation-Exchange-Capacity | | - | - | 0.728 | - |
| % Base Saturation | | -0.711 | -0.780 | -0.881 | - |

n = 24 p =< 0.1%

the principal soil environmental variables (all correlation values being $<\pm 0.600$ and therefore not significant at the 0.1% confidence level). This might indicate the importance of a manganese fraction in retaining Cd and Zn in the soil.

%B.S. would appear to be an important soil environmental variable which was related to the distribution of EXCH Cd, Zn and also Cu. pH related variables (pH, $\Sigma H^+$ and %B.S.) were all significantly important in producing relatively high coefficients with EXCH Cd, Zn and Cu. Depth also appeared to be associated with Zn and Cu distributions. In addition, organic matter (%C and bulk density) seemed to be associated with EXCH Cu. EXCH Cu distribution would appear to reflect those of EXCH Zn ($r = 0.938$) and EXCH Cd ($r = 0.949$), and hence it also correlated well with the same group of independent variables. However, EXCH Pb was significantly correlated with only three variables, two of which were MTOT Pb and NRES Pb. These variables (including NRES Fe) were depth related variables. EXCH Pb did not correlate well with any of the soil environmental variables - the variable with which it was best relates to was depth ($r = -0.592$).

## (B) Correlation of Non-Residual Heavy Metals with Various Soil Variables

Refer to Sections 3.6.3(A) and 3.6.4(A) for conditions and soil variables. The results are given in Table 3.6.6. The distributions of NRES Cd, Zn, Cu and Pb were very much reflected by the distributions of EXCH Cd, Zn, Cu and Pb respectively. This is advocated by the very high correlation coefficients that exist between EXCH and NRES metals. Hence much of what was mentioned in Section 3.6.4(A) holds true for this section.

## (C) Stepwise Multiple Regression of Easily Exchangeable / Non-Residual Heavy Metals on Six Principal Soil Environmental Variables

As in Section 3.6.3(C), six principal soil variables have been considered in order to explain the variation in the distribution of EXCH and NRES heavy metals in soil at Hallen Wood. The results are presented in Table 3.6.7.

## Table 3.6.7 Multiple Relationships Between Exchangeable and Total Extractable Cd, Zn, Cu and Pb Concs. (mg/kg) of Hallen Wood Soils and certain Soil Variables, according to Stepwise Regression Analysis

"Independent" variables : Depth, pH, % Carbon, Exchangeable $H^+$, Cation Exchange Capacity (C.E.C.) and % Base Saturation (%B.S.)

| | Exchangeable | | | Total Extractable | | |
|---|---|---|---|---|---|---|
| | Step no. Variables Entered | Multiple $100r^2$ | Simple r | Step no. Variables Entered | Multiple $100r^2$ | Simple r |
| Cd | 1. % B.S. | 58.18 | -0.763 | 1. pH | 54.00 | -0.735 |
| | 2. Exch. $H^+$ | 67.13 | 0.715 | 2. C.E.C. | 63.14 | 0.585 |
| Zn | 1. % B.S. | 63.21 | -0.795 | 1. % B.S. | 60.80 | -0.780 |
| | 2. C.E.C. | 72.54 | 0.563 | 2. C.E.C. | 69.41 | 0.555 |
| Cu | 1. % B.S. | 64.89 | -0.806 | 1. % B.S. | 76.66 | -0.881 |
| Pb | 1. Depth | 35.07 | -0.592 | 1. Depth | 36.69 | -0.606 |

---

The chief feature in Table 3.6.7 would appear to be the importance of %B.S. and pH in explaining the distribution of EXCH and NRES Cd, Zn and Cu. Depth appears to be the most important variable that would explain the variation in the EXCH/NRES Pb. However, Exch.$H^+$, C.E.C., depth, pH and %B.S. were all quite closely intercorrelated. Partial correlations indicate that, in general, a combination of variables in conjunction with depth were associated with the distribution of heavy metals down the Hallen profile. However, the Cd distribution appeared to be influenced primarily by soil acidity:

| Variables | | Correlation | Variable | Correlation | |
|---|---|---|---|---|---|
| $r_1$ | $r_2$ | $r_{12}$ | $r_3$ | $r_{123}$ | |
| EXCH Cd, | % B.S. | -0.763 | pH | 0.198 | N.S. |
| EXCH Cd, | % B.S. | -0.763 | depth | 0.487 | * |
| EXCH Cd, | % B.S. | -0.763 | % C | 0.576 | * |
| EXCH Cd, | % B.S. | -0.763 | C.E.C. | 0.618 | * |
| EXCH Cd, | % B.S. | -0.763 | Exch.$H^+$ | 0.574 | * |

| | | | | |
|---|---|---|---|---|
| NRES Cd, pH | -0.735 | % B.S. | 0.264 | N.S. |
| NRES Cd, pH | -0.735 | depth | 0.541 | * |
| NRES Cd, pH | -0.735 | % C | 0.433 | * |
| NRES Cd, pH | -0.735 | C.E.C. | 0.662 | * |
| NRES Cd, pH | -0.735 | Exch.$H^+$ | 0.486 | * |

* = p<5%, N.S. = p>5%

### 3.6.5. Discussion of Haw and Hallen Wood Results

There were certain features that both Hallen and Haw Wood shared as regards the availability of heavy metals in their soil profiles. The single most important fraction in the soils was the RES fraction. In this study, RES also comprised the Fe / Mn oxide and organo-residual fractions. Most of the work carried out using sequential extraction procedures agrees with this finding for both soils and sediments. In conjunction with this it is clear that there was little NRES Pb and Cu in either of the soil profiles despite the pHs for Hallen soil being <pH5 in the top half of the profile. Organic matter also appeared to play an important role in reducing the availability of the metals especially in the L, F, H and 0-1cm layers of both soils - this being the result of the high affinity that these metals have for organic matter (Hodgson 1963, Bloomfield *et al.*1976, Jones and Jarvis 1981). The proportion of NRES metals in both Haw and Hallen soils, in relation to their respective MTOT metals, decreased in the following sequence:

$$Cd > Zn > Cu = Pb$$

This order of mobility / bioavailability is in concordance with other field observations on the general mobility of these heavy metals in soils (Korte *et al.* 1976, Martin and Coughtrey 1987, Miller *et al.*1983, Scokart *et al.*1983). The Cu organic-bound fraction, SH, formed an important component of NRES in the soils (see Figs.3.6.3 and 3.6.5). This reflects the findings of others (e.g. Harrison *et al.*1981, Hickey and Kittrick 1984, Kuo *et al.*1983, McLaren and Crawford 1973a, Miller *et al.*1986) and is consistent with our knowledge of the chemical behaviour of Cu in soils (Harrison 1987). Also within both soils, of the NRES Pb and Cu, the AA or (AA + SH) fractions were proportionally

dominant which perhaps reflects the relative immobility of these two metals in the soils.

Further scrutiny of the data indicates that there were features that were not catholic to both soils and which were probably influenced by differences in, amongst other things, soil pH. Perhaps the most striking feature was the increased NRES Zn and especially Cd in Hallen Wood compared to Haw Wood (see Figs.3.6.2 and 3.6.4). Approximately 20-25% of the Cd in Hallen Wood soil was in EXCH form to 36cm (see Fig.3.6.4) depth which would suggest that this metal was extremely mobile under the conditions that existed in Hallen Wood.

Table 3.6.8 gives a few examples of studies that have looked at 2.5% HOAc extractable metals in soils. The large survey by Archer and Hodgson (1987) unfortunately recorded measurements in $mg/dm^3$ of soil. If the average bulk density of the soils was taken to be in the order of $\pm 1.0 g/cm^3$ then the concentrations recorded would not be far removed from equivalent concentrations in mg/kg. Suffice to say that in Hallen Wood, levels of Cd and Zn extracted to 36cm depth were up to 4.3 mg/kg for Cd, and >100 mg/kg (up to 135 mg/kg) for Zn (see Fig.3.6.8). Cd, especially, should be a matter for concern as Hallen extractable values (up to 4.3 mg/kg at depth) are greater than the "normal range" of total Cd (MTOT) of <1.0-3.9 mg/kg recorded by Archer and Hodgson (1987). Furthermore, 2-3.5 mg/kg of Cd were in an exchangeable form (WA + AN + Cc) to 41cm depth in the Hallen soil (see Fig.3.6.5). This would suggest that Cd in Hallen soil was potentially very mobile / bioavailable and hence could have been potentially phytotoxic to plants and other soil organisms. Haw Wood achieved comparable levels of Cd (and Zn) only in the top 6cm of soil. The high exchangeability of Cd has been evident in other studies (Bradley and Cox 1987, Hickey and Kittrick 1984, Kuo *et al.*1983).

Haw / Hallen Cu, in Table 3.6.8, was comparatively low in availability. The range of Haw / Hallen Cu was less than that covered in unpolluted Scottish soils (Berrow and Mitchell 1980). Haw / Hallen Pb data in Table 3.6.8 superficially appear to be quite large; but the higher range for Pb is heavily skewed towards the litter layers and topsoil values of both woodlands. More typically, the range for Pb in both woodland soils (excluding the top 6cm of soil and L, F, H layers) was 0.02-4 mg/kg.

All four metals in Hallen soil were generally more available (NRES) than in Haw soil (see Fig.3.6.6); and despite Haw Wood generally having about equal or greater MTOT from the L, F, H layers down to 11 depth (see Table 3.6.9),

**Table 3.6.8 Extractable (2.5% HOAc) trace element contents of Haw Wood and Hallen Wood soils compared to data for soils in England, Wales and Scotland.**

Archer and Hodgson (1987) :

| | Cd (HOAc) mg $dm^{-3}$ | Zn (HOAc) mg $dm^{-3}$ | Cu (HOAc) mg $dm^{-3}$ | Pb (HOAc) mg $dm^{-3}$ |
|---|---|---|---|---|
| Log-Derived Mean | 0.2 | 6.0 | 1.2 | 1.4 |
| Median | 0.2 | 5.8 | 1.0 | 1.6 |
| Overall Range | <0.2-4.3 | 0.1-138 | 0.2-34 | <0.1-1080 |
| "Normal Range" | <0.2-1.9 | 1.3- 28 | 0.3- 5.1 | 0.13- 16 |
| No. of Samples | 1249 | 1364 | 356 | 1286 |

Berrow and Mitchell (1980) :

| | µg/g | µg/g | µg/g | µg/g |
|---|---|---|---|---|
| Overall Range | <0.01-0.27 | 0.58-21 | 0.14-6.1 | 0.01-0.97 |
| No. of Samples | 23 | 23 | 23 | 23 |

Jarvis and Jones (1980) :

| | µg/g |
|---|---|
| Overall Range | 0.022-0.110 |
| No. of Samples | 10 |

Haw Wood (1987) :

| | µg/g | µg/g | µg/g | µg/g |
|---|---|---|---|---|
| Overall Range | 0.047-7.495 | 0.476-243.41 | 0.195-0.601 | 0.02-11.84 |
| No. of Samples | 21 | 21 | 21 | 21 |

Hallen Wood (1987) :

| | µg/g | µg/g | µg/g | µg/g |
|---|---|---|---|---|
| Overall Range | 0.133-5.431 | 1.13-186.063 | 0.121-1.794 | 0.06-67.71 |
| No. of Samples | 28 | 28 | 28 | 28 |

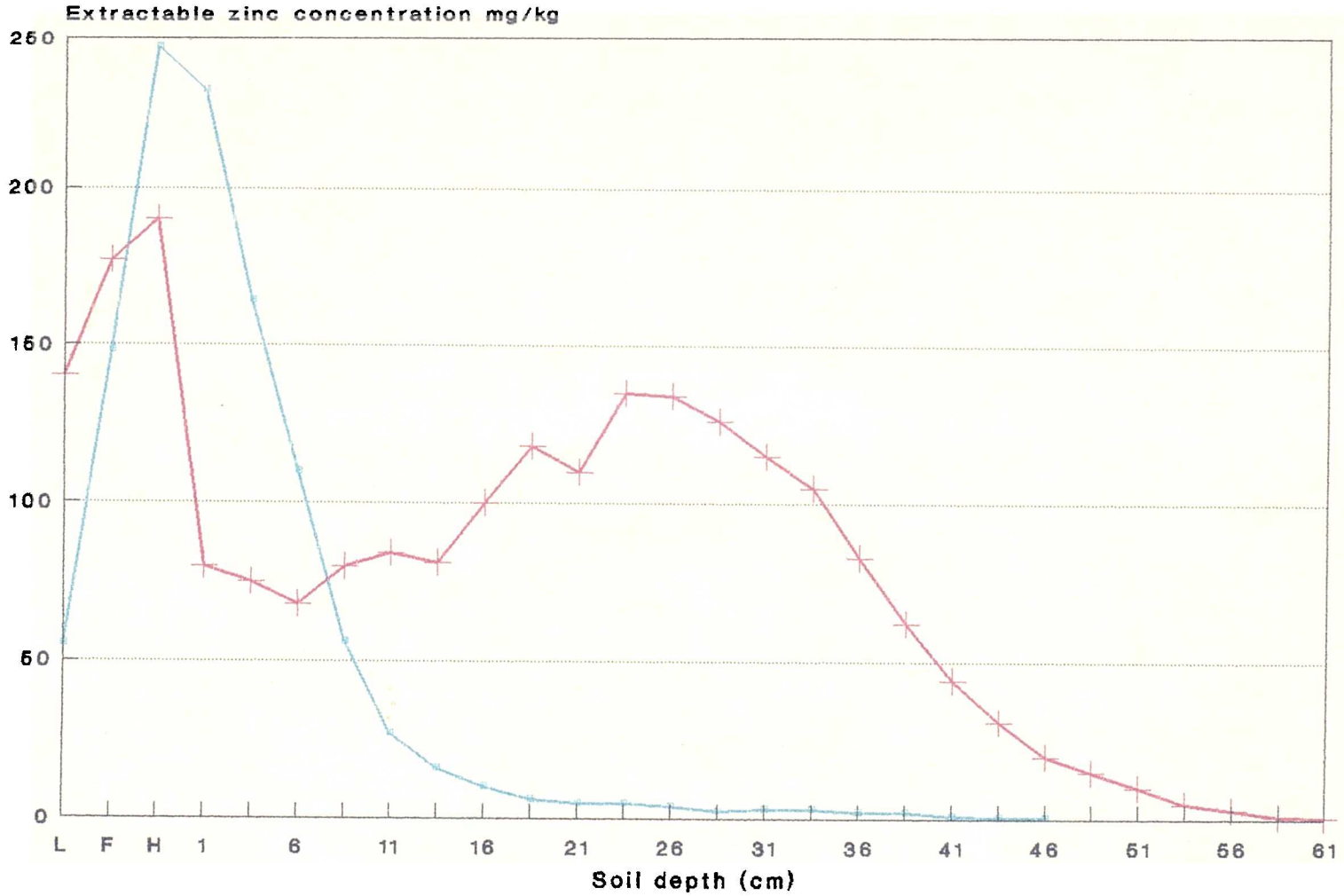


Fig.3.6.6a NRES Zinc in Haw and Hallen Wood 1987 Soil Profiles.

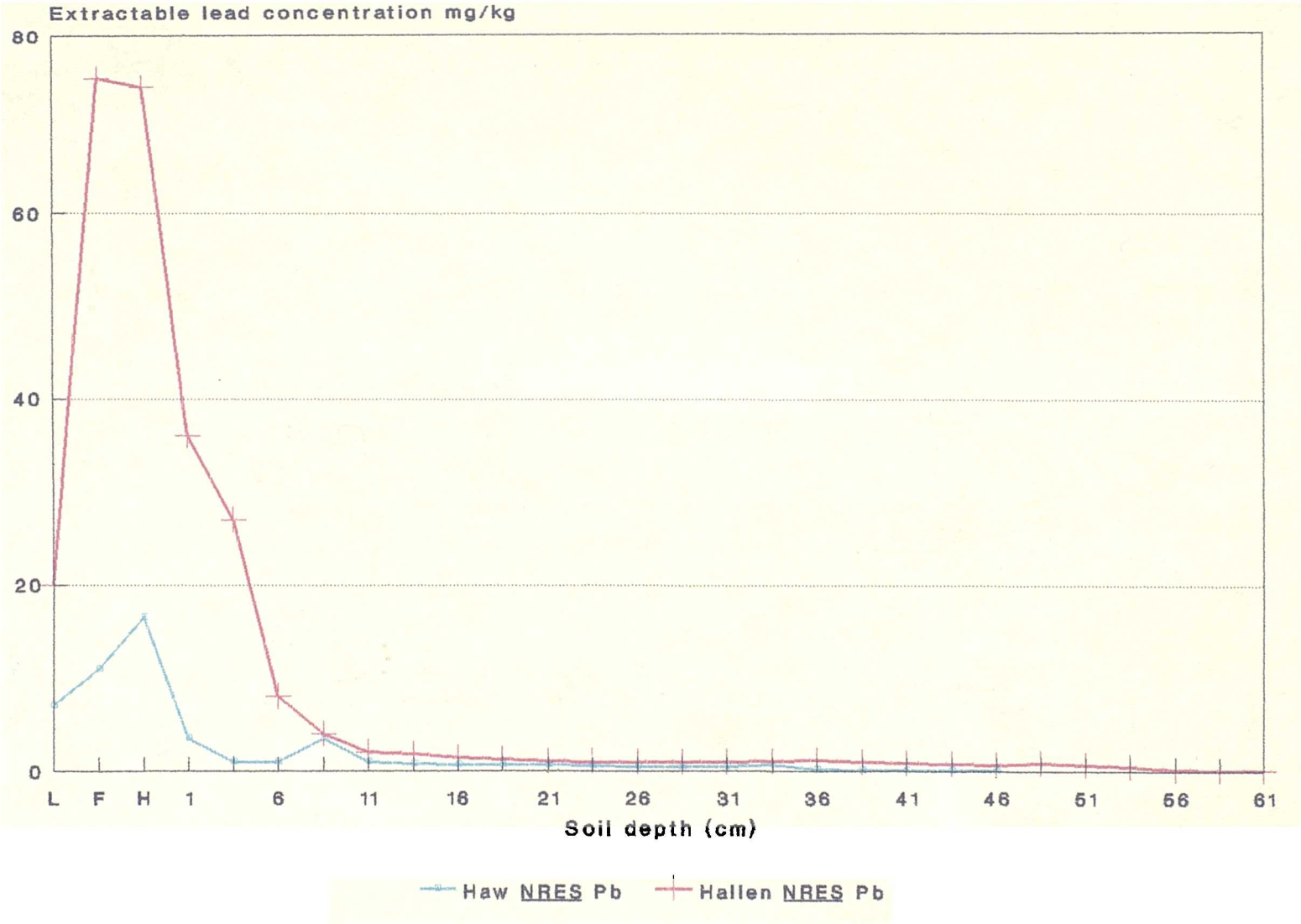


**Fig.3.6.6b NRES Lead in Haw and Hallen Wood 1987 Soil Profiles.**

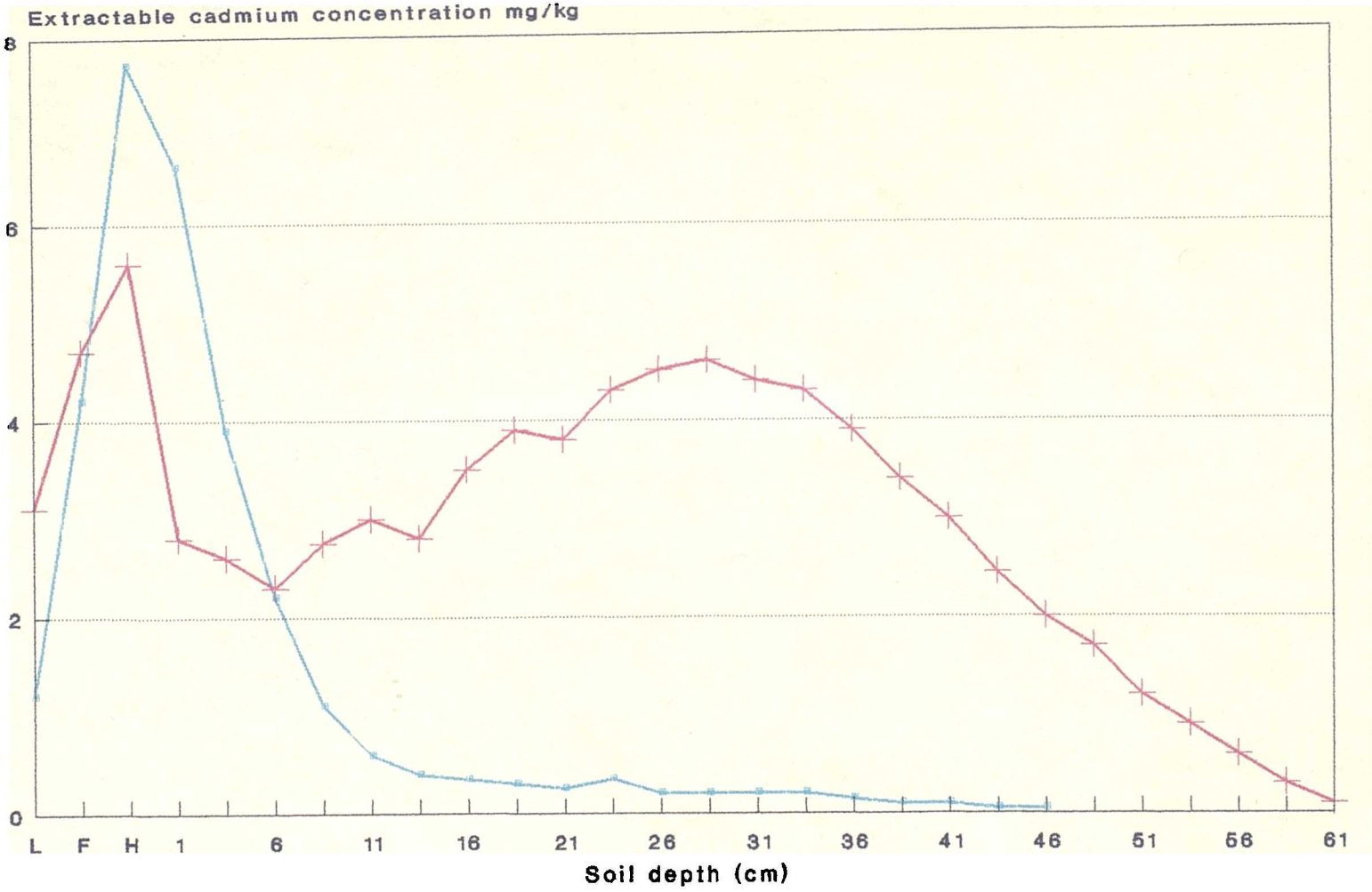


**Fig.3.6.6c NRES Cadmium in Haw and Hallen Wood 1987 Soil Profiles.**

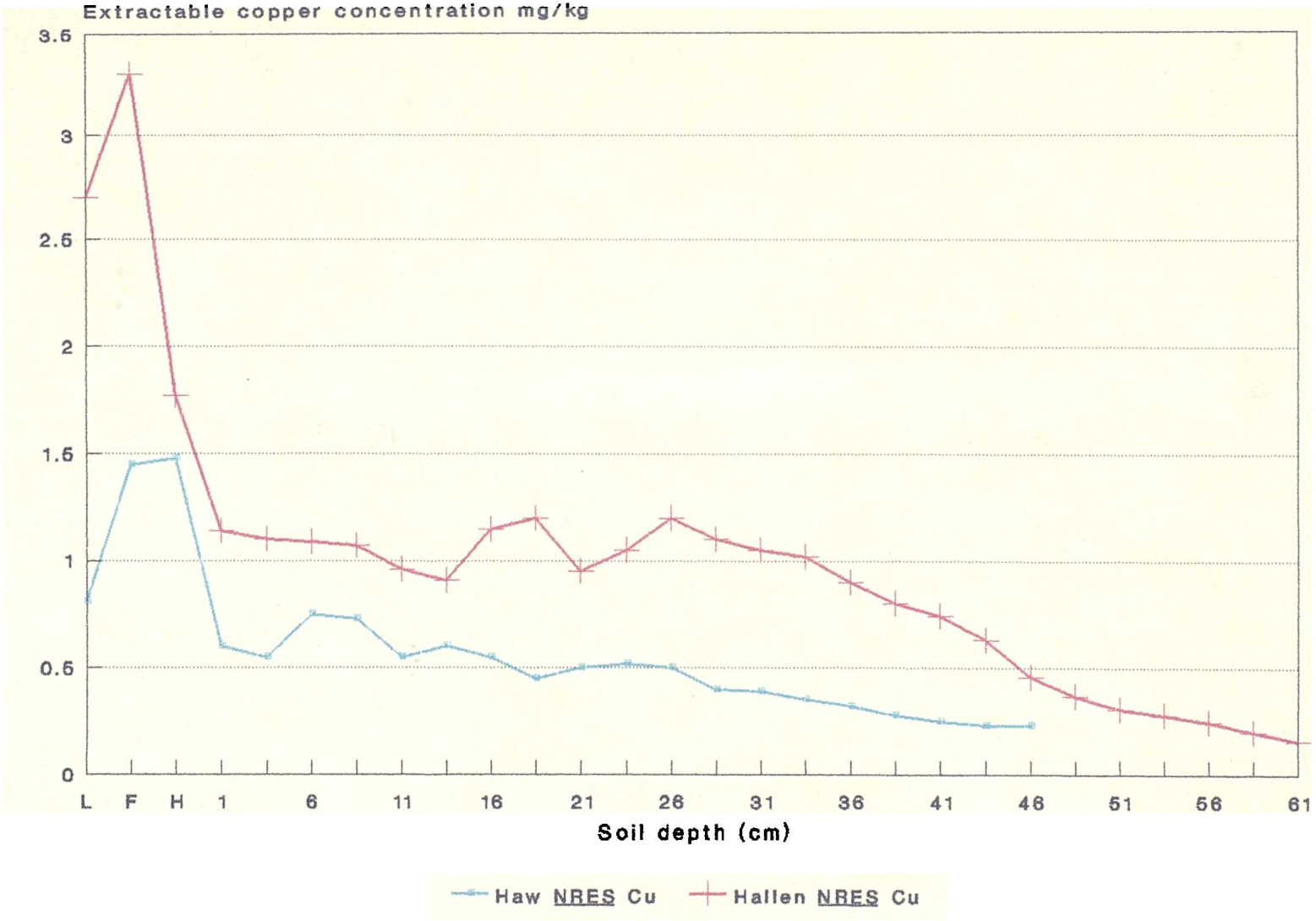


Fig.3.6.6d NRES Copper in Haw and Hallen Wood 1987 Soil Profiles.

**Table 3.6.9 Total Metal Concentration and Total Extracted Metal Data for the Top 11cm of Haw/Hallen Wood Soils (continued on page 157).**

| | Cadmium | | | | Zinc | | | |
|---|---|---|---|---|---|---|---|---|
| | Haw 1987 | | Hallen 1987 | | Haw 1987 | | Hallen 1987 | |
| | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. |
| L | 18.7 | 6.43 | 28.6 | 10.91 | 1309 | 4.09 | 1889 | 7.47 |
| F | 51.6 | 8.07 | 33.2 | 14.14 | 3009 | 4.92 | 1864 | 9.54 |
| H | 73.4 | 10.46 | 37.2 | 14.95 | 3388 | 7.31 | 1714 | 11.11 |
| 0-1 | 34.8 | 19.67 | 10.5 | 26.73 | 1690 | 13.70 | 613 | 13.62 |
| 1-3.5 | 20.0 | 19.37 | 4.6 | 56.22 | 1234 | 13.25 | 334 | 23.16 |
| 3.5-6 | 11.2 | 20.02 | 4.3 | 53.11 | 848 | 13.33 | 306 | 22.31 |
| 6-8.5 | 5.3 | 22.11 | 4.1 | 65.19 | 478 | 11.77 | 291 | 27.16 |
| 8.5-11 | 2.8 | 23.09 | 4.9 | 61.31 | 333 | 8.19 | 318 | 26.37 |

**Table 3.6.9 (cont.).**

| | Lead | | | | Copper | | | |
|---|---|---|---|---|---|---|---|---|
| | Haw 1987 | | Hallen 1987 | | Haw 1987 | | Hallen 1987 | |
| | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. | Total Conc. µg/g | % Total Extr. |
| L | 924 | 0.74 | 2172 | 0.93 | 110 | 0.74 | 263 | 1.03 |
| F | 2341 | 0.45 | 4798 | 1.57 | 236 | 0.61 | 197 | 1.66 |
| H | 3184 | 0.51 | 4051 | 1.83 | 174 | 0.85 | 165 | 1.08 |
| 0-1 | 460 | 0.82 | 738 | 4.89 | 45.2 | 1.30 | 43.9 | 2.60 |
| 1-3.5 | 147 | 0.51 | 195 | 8.73 | 32.8 | 1.75 | 23.6 | 4.72 |
| 3.5-6 | 120 | 0.62 | 131 | 5.95 | 33.0 | 2.31 | 21.9 | 4.99 |
| 6-8.5 | 168 | 1.40 | 83 | 5.13 | 30.4 | 2.41 | 19.8 | 5.42 |
| 8.5-11 | 61 | 1.15 | 67 | 3.24 | 28.0 | 1.94 | 20.4 | 4.37 |

Total Extracted Metal Data are the sum of metal concentrations (WA + AN + Cc + AA + SH), expressed as a percentage of the total concentrations (ie. concentrated nitric acid digests)

overall, proportionally more metal was extracted from the equivalent Hallen soil horizons.

In terms of EXCH metals in Hallen Wood mineral soil, Cd and Zn have at least 10% of their MTOT in this very mobile/bioavailable state to respective depths of 51cm and 31cm (Fig.3.6.4). This might suggest that Cd was more mobile than Zn under the prevailing soil conditions. However, purely in terms of NRES metals (Fig.3.6.5), there was proportionally as much, if not more, Zn extracted as EXCH metals in relation to Cd. In fact, proportionally, the solid phase metals of Zn within the NRES fraction of Fig.3.6.5 closely reflects the proportional distribution of Cd. This factor might help explain how Zn MTOT profiles have generally reflected those of Cd over the years (see Chapter 2, Section 3.3). Certainly within the 1987 Hallen mineral soil profile, the MTOT profiles of both metals correlate with each other at $r = 0.968$, which suggests that movement of both metals has occurred in close tandem.

The correlation data (and regression data) in Tables 3.6.2-3.6.7 bring to light certain features that may be allied with or contributory factors towards heavy metal availability in the two soils. Some of the highest correlation coefficients are associated with the close geochemical behaviour that Cd and Zn share in both soils. The geochemical link between Cd and Zn (Hamilton 1987) has been apparent in a sequential extraction study by Elsokkary and Låg (1978). One surprising anomaly that the Zn coefficients show is their lower correlation values for Hallen soil between MTOT Zn and NRES Zn ($r = 0.746$) / EXCH Zn ($r = 0.702$); and yet MTOT Cd correlates much better with NRES Zn ($r = 0.919$) and EXCH Zn ($r = 0.892$). This perhaps corresponds to the fact that Zn was the one heavy metal that had significantly higher concentrations in its various phases (i.e. solution, exchangeable etc.) than Cd, Cu and Pb. In quantitative terms, Zn was far in excess of the other three metals, and in the Hallen soil system almost took on the guise of a minor element such as Mn rather than a trace element (see Fig.3.6.8). This means that with respect to its geochemical partner Cd, EXCH/NRES Zn mirrored EXCH/NRES/MTOT Cd (see Tables 3.6.5 and 3.6.6); but because the pH increased and sharply rose at depth in the Hallen soil (see Fig.2.3.12, Chapter 2, Section 3.3) it seems inevitable that there would be a greater amount of occluded and precipitated Zn at depth. Therefore, the greater quantity of NRES Zn in relation to NRES Cd would appear to have been the likely cause for the enhancement of the Zn MTOT "wave" with depth in relation to the Cd MTOT "wave" (c.f. Fig.2.3.5a and 2.3.5c, Chapter 2, Section 3) such that RES Zn (and MTOT Zn) became proportionally much greater deeper down the profile (see Fig.3.6.4). In

Fig.3.6.4 it is noticeable that Cd behaved similarly to Zn; but the discrepancy was not of the same order of magnitude, so that a significant portion of the MTOT Cd was still in an NRES (available) form.

It is worth mentioning at this point that of the NRES Cd and NRES Zn (see Fig.3.6.5), the proportional reduction in total exchangeable Cd ($\Sigma$ WA + AN + Cc) was not as severe as total exchangeable Zn from 41cm depth and deeper. This might indicate the potentially greater mobility of Cd in relation to Zn at depth and at higher pH values. Nevertheless, the original background concentrations of the soil should be considered: it might be that proportionally more of the Cd in the deeper soil horizons originated from aerial contamination due to very low natural background concentrations in the soil, whereas Zn might have had more metal naturally *in situ* within the soil in the first place such that proportionally less Zn was derived from aerial contamination. However, in Haw Wood, all Zn and Cd variables highly inter-correlate. Perhaps this is a product of the low degree of acidification in the Haw Wood system (see Fig.3.6.9) and hints at how slowly the Haw Wood Cd and Zn profiles are evolving in comparison to Hallen profiles.

There are indications that NRES and EXCH Cu were affected by similar soil variables that were associated with Cd and Zn availability. This assertion is most lucidly conveyed by the correlation coefficients for Hallen Wood (see Tables 3.6.5 and 3.6.6). EXCH and NRES Cu are highly, positively correlated with the distribution of their counterparts in EXCH Cd ($r = 0.949$, $r = 0.925$), NRES Cd ($r = 0.926$, $r = 0.880$), EXCH Zn ($r = 0.938$, $r = 0.943$) and NRES Zn ($r = 0.948$, $r = 0.935$), including the MTOT Cd ($r = 0.930$, $r = 0.894$). This may raise the supposition that Cu was relatively mobile in the Hallen profile in comparison to Zn and Cd. Inspection of Fig.3.6.6a-d confirms that there was quantitively more Cu in an NRES form in Hallen Wood compared to Haw Wood by a factor of 1.5 to 3 at most depths. However at soil depths greater than 11cm, Cd and Zn NRES concentrations in Hallen Wood were far in excess of NRES metal in Haw Wood.

Due to the high quantitative availability of Cd and Zn in relation to their natural background MTOT concentrations (see Chapter 2, Section 2.2) in conjunction with the lower pH (Chapter 2, Section 3.3, Fig.2.3.12) and higher EXCH acidity of Hallen soil (Fig.3.6.9), "wave" distributions of their MTOT concentration profiles have developed and evolved with time (see Chapter 2, Section 3.3). Despite it's available forms reflecting the distribution of Cd and Zn available forms in Hallen Wood, Cu presumably had not a high enough quantitative throughput of available Cu in relation to it's natural background

concentrations to form comparable "wave" features in its MTOT profiles. One could surmise that if the aerial input of Cu into the Hallen system was increased and/or the high affinity that Cu is known to have for organic matter was less, then a distinct Cu "wave" would be evident in the Hallen soil system. It might also be conjectured that an increase in the aerial input of Cu into the Hallen system would create Cu distributions that would bear close alliance with those of Pb because, in general, Cu and Pb are recognised as being more immobile than Cd or Zn (Korte *et al.* 1976, Miller *et al.* 1983, Scokart *et al.* 1983; see Chapter 2, Section 2.2). One explanation for Hallen EXCH/NRES Cu reflecting the EXCH/NRES Cd and Zn (considering that Cu is thought of as relatively immobile in relation to Cd and Zn) is suggested by Lepp (1979): i.e. where Zn occurred in excess in soils, displacement of other metals such as Cu could occur e.g. where excess Zn could outweigh the stability effect of Cu for organic matter.

However, Hallen Pb appeared to be very different to the other three heavy metals with regards to its correlation coefficients (Table 3.6.5 and 3.6.6), which was probably a result of it's high aerial input into the woodland system in combination with it's low mobility (see Fig.3.6.6). Extremely high MTOT Pb in litter (see Chapter 2, Section 3.3) have led to high Pb throughput / movement in the Hallen Wood topsoil such that a distinct concentration gradient was still maintained in it's EXCH/NRES forms (eg. see Fig.3.6.6). Therefore, despite the exclusion of the L, F, H and 0-1cm layers, Pb correlates best upon its own variables (Pb MTOT, Pb EXCH, Pb NRES) and was possibly associated with the weathering and production of extractable Fe (see Tables 3.6.5 and 3.6.6).

In Haw Wood, neither EXCH/NRES Pb nor Cu possessed the steeper concentration gradients that EXCH/NRES Cd and Zn both shared in the mineral topsoil (see Fig.3.6.6): this would explain, in part, why EXCH/NRES Cu in Haw Wood do not correlate as highly with EXCH/NRES Cd and Zn (Table 3.6.2 and 3.6.3) as they did in Hallen Wood (Table 3.6.5 and 3.6.6). However, unlike Haw EXCH/NRES Pb, Haw EXCH/NRES Cu do correlate very well with organic matter (see Tables 3.6.2 and 3.6.3) as, indeed, do EXCH/NRES Cd and Zn.

**Table 3.6.10 Correlation Coefficients between Organically Bound (SH) Metals (on humic substances) and Water Soluble (WA), Easily Exchangeable (EXCH) and Non-Residual (NRES) Metals in Hallen Wood Soil**

| | | Cd SH | Zn SH | Cu SH | Pb SH |
|---|---|---|---|---|---|
| Cd | WA | 0.360 | - | - | - |
| | EXCH | 0.401 | - | - | - |
| | NRES | 0.380 | - | - | - |
| Zn | WA | - | 0.629 | - | - |
| | EXCH | - | 0.734* | - | - |
| | NRES | - | 0.738* | - | - |
| Cu | WA | - | - | 0.847* | - |
| | EXCH | - | - | 0.818* | - |
| | NRES | - | - | 0.932* | - |
| Pb | WA | - | - | - | 0.779* |
| | EXCH | - | - | - | 0.853* |
| | NRES | - | - | - | 0.866* |

n = 24 * : p < 0.1%

---

Two distinct patterns of metal leaching in forest soils have been identified (Bergkvist and Folkeson 1988, Bergkvist *et al.*1989):

(a) A crucial role is played by soluble organic acids, predominantly humic substances associated with the mineralisation of organic matter in the topsoil, i.e. transport of organic acids through the A horizon.

(b) An association with soil acidity - a gradual release of metals from the mineral soil and an increase in soil solution concentration of metals through the B horizon.

Patterns (a) and (b) appeared to correspond to the pattern of development in Haw Wood and Hallen Wood soils respectively, especially in relation to the more mobile heavy metals, Cd and Zn. Bergkvist (1986, 1987) suggested that Pb and Cu tend to be associated with the leaching of organic matter in soils. Table 3.6.10 indicates that the distributions of other available fractions of Cu


**Fig.3.6.7 EXCH Potassium and Zinc in the Hallen Wood 1987 Profile.**

**Table 3.6.11 Most Probable Hydration Numbers according to Ulrich, and Mean Effective Diameters (d) in Angströms as given by Kielland (after Wiklander 1964)**

| Ion | $H^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Ba^{2+}$ |
|---|---|---|---|---|---|---|---|---|
| $H_2O$/ion | 4 | 6 | 4 | 2.5 | 2 | 9-13 | 8-10 | 6-8 |
| d | 9 | 6 | 4.3 | 3 | 2.5 | 8 | 6 | 5 |

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and Pb in Hallen soil appear to be closely associated with their extractable humic/fulvic fractions.

Furthermore, there were two other factors associated with the elements K and Mn that should be considered. EXCH K was inextricably highly correlated with the distributions of EXCH/NRES Cd, Zn and Cu in both Haw and ,more especially, Hallen Wood (see Tables 3.6.2, 3.6.3, 3.6.5, 3.6.6 and Fig.3.6.7). Research by Abrahamsen and co-workers and Morrison (1983) would suggest that K is less sensitive to soil acidification in relation to the other major cations Ca and Mg (see Bergkvist 1986). The alkali and alkaline earth metals (e.g. $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) are held in soils principally by cation exchange reactions involving the soil particles, whereas the larger monovalent cations (e.g. $K^+$, $Rb^+$ and $Cs^+$) can be adsorbed specifically by clay minerals, such as clay mica and vermiculite, and to a lesser extent by smectite (Evans 1989, Jackson 1964, Talibudeen 1981). $K^+$ has a large enough ionic radius to fit into the 12-coordinated positions formed by adjacent ditrigonal basal oxygen atoms of tetrahedral sheets of expandable clay minerals (Evans 1989); and mineral K has been reported as being related to the clay content of soils (Al-Kanani *et al.*1984, Sharpley 1989). As $K^+$ has a low hydration energy, it can lose its associated water molecules so that its effective diameter is much reduced (see Table 3.6.11 for diameters). The relative affinity that $K^+$ has for mica clays is illustrated by an investigation of Schachtschabel in 1940 on the release of $NH_4^+$ from biotite by different chlorides of metals (Wiklander 1964):

| Conc. (N) | $NH_4^+$ Biotite |
|---|---|
| 0.005 | Li < Na < Mg < Ca < Sr < K < Cs < Ba < Rb < H |
| 0.1 | Li < Mg < Na < Ca < Sr < Ba < Cs < Rb < K < H |

It is possible that the distributions of Hallen/Haw EXCH K (Fig.3.6.7 and 3.6.8) were an indication of proton adsorption and / or alumino-silicate weathering on clay colloids especially in the upper section of the Hallen profile. This, in conjunction with appreciable leaching of K from plant material / litter layers might have been accountable for the EXCH K distributions. Therefore, one suggestion for the distribution of EXCH K reflecting the distributions of available Cd, Zn and Cu is because of it's ability to be specifically adsorbed upon clays, whereas metals such as Mg and Ca are more easily leached; hence the acidified Hallen profile did not produce an exchangeable Mg and Ca "wave" distribution as it did for K (see Fig.3.6.8b). Again, as was the possible case with Cu, it cannot be ruled out that the EXCH K has been affected by heavy metal displacement. It has been reported that by increasing additions of heavy metals in soil, such as Cd or Cu up to 400 mg/kg, an increase in the fractional saturation of K upon the exchange phase can occur (Yang and Skogley 1989). Zn occurred at high concentrations to depth in the Hallen soil and in the Haw topsoil. Other factors such as Haw/Hallen organic matter distribution and any phytotoxic effect that the soil levels of heavy metals such as Cd and Zn might provide should, perhaps, also be considered.

Mn related variables also appear to correlate highly with EXCH/NRES heavy metal distributions in Haw/Hallen soils. NRES Mn/Fe and EXCH Mn were important variables that correlated with Pb in Haw and Hallen Wood (Tables 3.6.2, 3.6.5, 3.6.6). It is possible that the weathering of Fe/Mn oxides in these soils would have aided the leaching of Pb down the profiles. EXCH/NRES Cu correlated very well with EXCH/NRES Mn, especially in Hallen Wood (Tables 3.6.3, 3.6.5, 3.6.6). Cu is known to have a great affinity for Mn oxides (Tyler 1981). The fact that Cd and Zn also were related to Mn distributions in Hallen Wood corroborates the idea that Mn oxides might have had some influence on heavy metal soil distributions. This is further supported by the high correlation coefficients that the Cd and Zn variables have with total soil Mn concentrations at Hallen. It seems likely that the MTOT Mn concentrations were analogous to the distribution of Mn oxides within the profile. Furthermore, metals such as Cu and Zn are often associated with Mn nodules (Taylor and McKenzie 1966) and factors that would affect the solubility of Mn concretions would also affect the mobility of the associated metals (Bergkvist 1986, Bergkvist and Folkeson 1988). Therefore, weathering of Mn oxides might have been enough to provide extra Cu for EXCH/NRES Cu

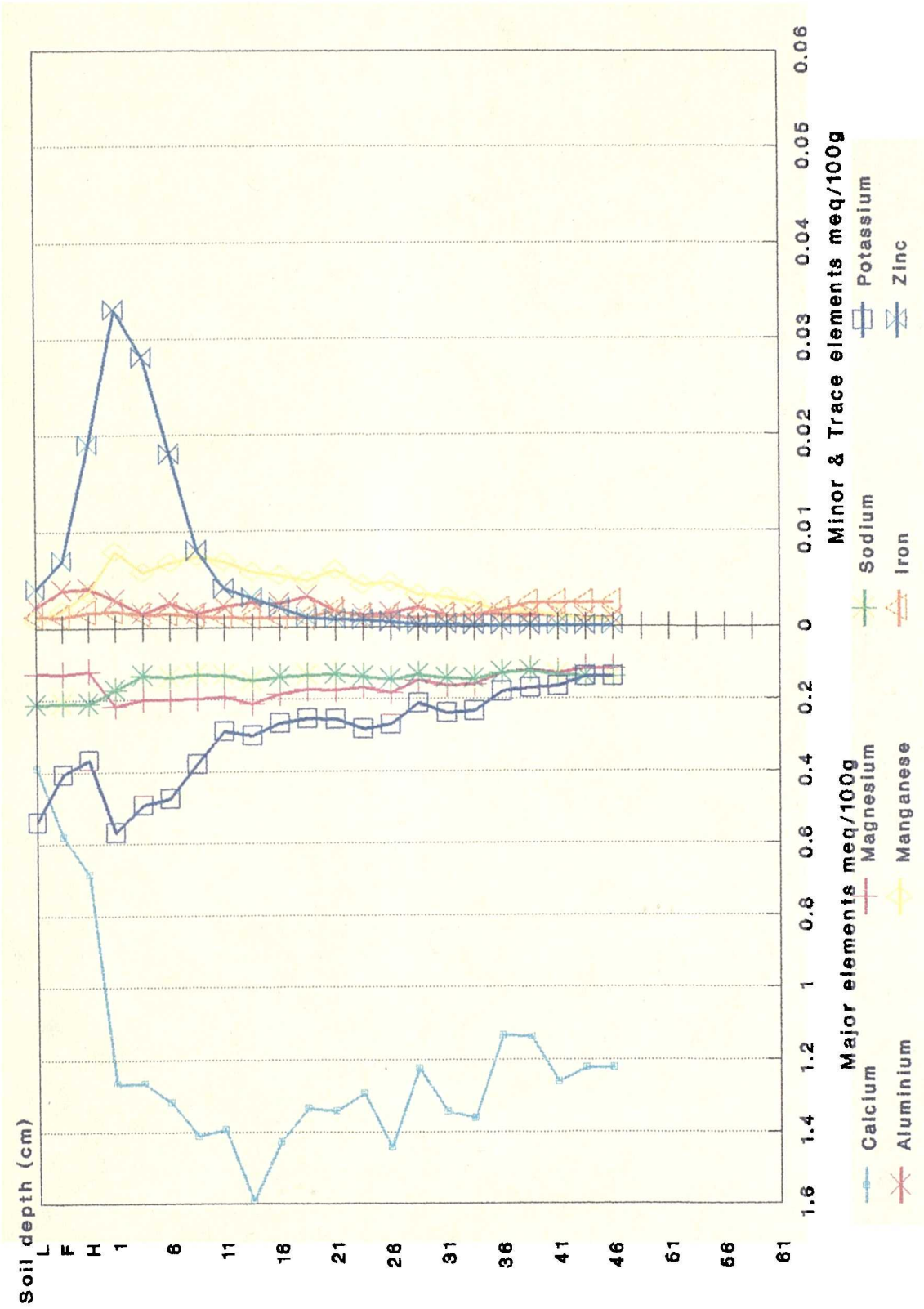



Fig.3.6.8a EXCH Metals in Haw Wood Soil

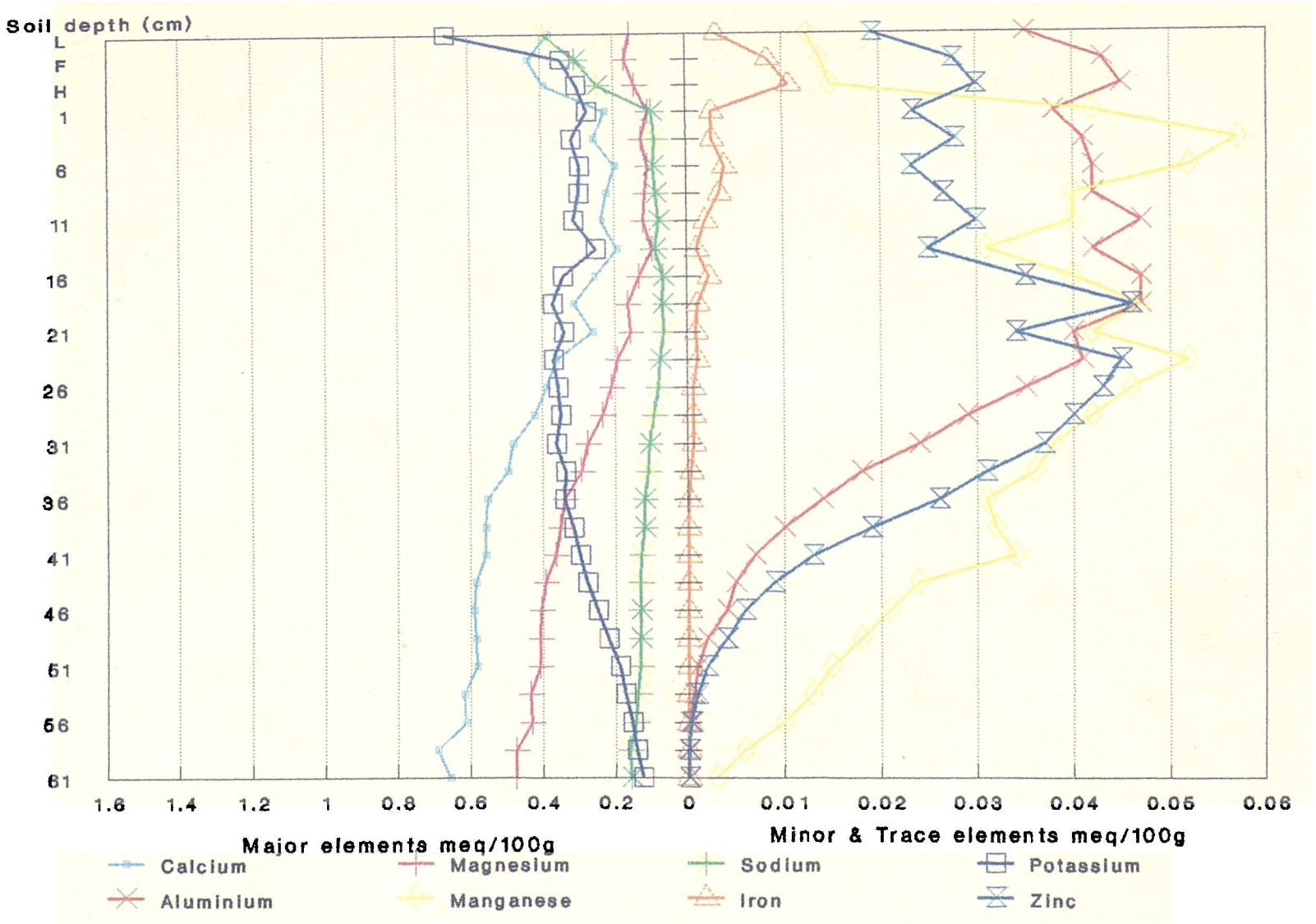



Fig.3.6.8b EXCH Metals: Hallen Wood Soil

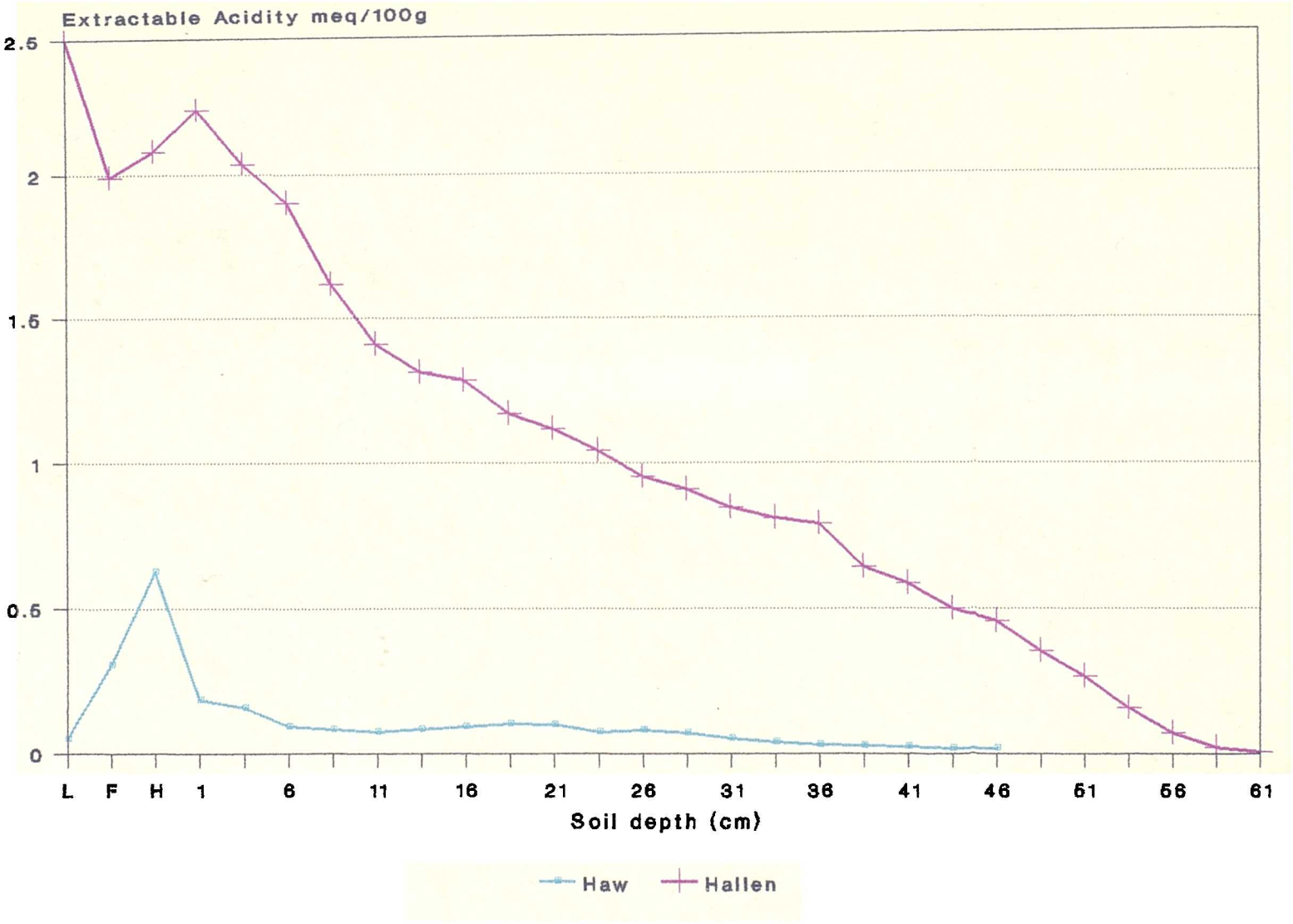



Fig.3.6.9 EXCH Acidity: Haw and Hallen 1987 Soil Profiles.

distributions to be highly correlated with EXCH/NRES Cd and Zn distributions in Hallen Wood.

Finally, it is interesting to note the relationships demonstrated between the distribution of water soluble anions and heavy metal distributions in EXCH/NRES forms (Tables 3.6.2, 3.6.3, 3.6.5, 3.6.6). Further details are provided in Chapter 4, Section 4.

## 3.6.6. Distribution of Easily Exchangeable Metals and Acidity in the Haw and Hallen Wood Soil Profiles

Fig.3.6.8a and Fig.3.6.8b illustrate the distribution of EXCH metals down both soil profiles. Zn (meq/100g) has been put on the graphs to illustrate how Zn (and Cd which is closely correlated to EXCH Zn) reacted in the two different soil systems. Three features that seem apparent are:

(a) $Ca^{2+}$ was the dominant EXCH metal in both profiles, but was much depleted in the top of the Hallen profile. The $K^+$ distribution was very unlike it's other group IA and IIA compatriots and appeared to have an EXCH distribution more akin to a heavy metal such as $Zn^{2+}$ (see also Fig.3.6.7).

(b) The metals Fe, Mn, Zn (and Cd) and Al were more exchangeable in the top half of the Hallen profile than the lower half, where they showed decreases with depth. Metals such as Ca and Mg increased with depth in the Hallen profile. In Haw Wood, there was comparatively little in the way of EXCH Fe, Mn, Zn and Al. However, high levels of Zn were present in the top of the Haw profile, signifying the accumulation of this metal in the topsoil from aerial deposition.

(c) The distribution of EXCH acidity might account for the distributions of the various EXCH metals (see Fig.3.6.9). Certainly in the Hallen profile, EXCH $H^+$ was probably influential in the production of EXCH Fe, Mn, Zn and Al in the top of the profile and contrastingly responsible for the displacement of Ca, Mg and Na from the top of the profile. The EXCH $H^+$ load in Hallen Wood was orders of magnitude greater than that of Haw Wood and could help explain the discrepancies which seem apparent in the EXCH cation distributions in Fig.3.6.8.

Changes in soil pH and base saturation (of which Ca is the dominant cation in most instances) are closely related (Billett *et al.*1990). Soil pH is largely

controlled by Ca, since it is the dominant base cation on exchange sites (Alban 1982). The pH of the 1987 Hallen Wood profile was pH4.0-5.0 to a depth of 31cm. This region of soil pH ($H_2O$) has been recognised as important in defining an aluminium / cation exchange buffer range (Ulrich 1980, 1983, 1986). The cation exchange buffer range is meant to respond mainly within the pH4.2-5.0 range (Ulrich 1983, 1986). This pH range is hallmarked by increased exchangeable $Mn^{2+}$ and $Al^{3+}$, reduced base saturation and increased leaching of the Group IA and IIA metals (Na, K, Mg and Ca) (Ulrich 1986). This is associated with the weathering of Mn oxides and clay minerals (Ulrich 1986). If the level of exchangeable Ca falls <5-10% of the C.E.C., then a physiological strain may be incurred upon microorganisms and plant roots (Ulrich 1983). In the Hallen profile, EXCH Ca was <10% of the effective EXCH C.E.C. meq/100g (as defined by the 0.1M $NH_4NO_3$ extractant) to a depth of 13.5cm in the mineral soil. Conversely, in Haw Wood, EXCH Ca was overwhelmingly dominant.

Titratable acidity of a soil is governed by the exchangeable protons and cation acids (ion species of Mn, Al and Fe, and heavy metals) (Ulrich 1983, Ulrich and Matzner 1986). The composition of the exchangeable cations is therefore the most informative way to characterise the actual acid/base status of a soil (Ulrich and Matzner 1986). In the course of a study by Bredemeir (1987), the predominant $H^+$ consuming reaction was $Al^{3+}$ dissolution; release of this potentially phytotoxic ionic species into the soil solution was generally accompanied by the depletion of exchangeable base cations in the soil. It seems likely that the increase EXCH Al in Hallen Wood, in comparison to Haw soil (Fig.3.6.8), was a natural response to the greater acidification within the former woodland soil (Fig.3.6.9; see Chapter 2, Section 3.4). Such a response in acidified soils has been reported widely (e.g. Billett *et al.*1990, Lilieholm and Feagley 1988, Ulrich *et al.*1980).

The distribution of EXCH K (Fig.3.6.8b) is intriguing, especially with respect to the Hallen profile, at it tends to be allied with the distributions of less mobile elements such as Zn and Mn, and not with Na, Mg and Ca. As early as 1937, Polynov had suggested that the relative mobility of K was less than that of Ca, Mg and Na (see Curtis *et al.* 1976). Morrison and Foster (1987) recognised that the relative leaching of base cations in weakly podsolised forest soils follows the order:

$$Ca > Mg > Na > K$$

Bergkvist (1986) found that concentrations and fluxes of Mg, Ca, Mn, Zn and Cd in a forest soil were significantly increased by addition of acidified throughfall waters; K was less affected. In Hallen and Haw soils, only 1-3% of the MTOT K was in an EXCH form compared to 15-30% of the MTOT Ca that was in an EXCH form. This is in close agreement with data quoted by Brady (1984) for a representative humid, temperate region, mineral soil. It serves to illustrate how much less available K is compared to Ca. K does not have as high an affinity for water of hydration as do other cations such as $Na^+$ and $Ca^{2+}$; and hence $K^+$ is easily dehydrated and its small size is such as to enable it to fit snugly between the silica sheets of adjoining layers in 2:1-type clay minerals (Brady 1984). Hallen and Haw Wood soils are dominated in their clay mineralogy by the 2:1 clay minerals montmorillonite, illite and micaceous chlorite (see Chapter 2, Section 1.4). Potential factors that might have affected the K distribution have been discussed in Section 3.6.5.

## 3.6.7. Discussion with Respect to Similar Studies

Fractionation schemes that have been used on relatively unpolluted soil systems containing Cd, Cu, Pb and Zn, indicate that most of these heavy metals are located in the residual-Fe/Mn oxide fractions (Iyengar *et al.*1981, McLaren and Crawford 1973a, 1974, McNeal *et al.*1985, Miller *et al.* 1986, Shuman 1979, 1985, Sims and Patrick 1978), with copper sometimes having a major fraction associated with organic matter.

A number of studies have looked at smelter emission heavy metal inputs of Cd, Cu, Pb and Zn onto soils and have used extraction techniques to assess mobility / availability of the metals. Some have used sequential extraction techniques e.g. Elsokkary and Låg (1978), Hickey and Kittrick (1984), Kuo *et al.*(1983), Miller and McFee (1983). The general consensus is that Cd is by far the most available / mobile metal. Generally the order of metal availability / mobility follows the order below:

$$\frac{\text{Exchangeable Metal in Soil}}{\text{Total Metal in Soil}} \% = Cd > Zn > Pb = Cu$$

Kuo *et al.*(1983) recorded up to 60% of Cd in an exchangeable form for some soils. Their data were recorded for no deeper than 30cm depth and were for Cd concentrations greater than 8 mg/kg. The four previous studies mentioned above were all carried out on sandy or sandy-loam soil types. In the 1987 Hallen Wood soil profile, up to 54% of the Cd was in an

exchangeable form (0.1M $CaCl_2$ extractable = WA + AN + Cc) at 31cm depth in a predominantly clay soil. Kuo *et al.*(1983) obtained their soils from gardens (as were the soils sampled by Hickey and Kittrick 1984), whilst Elsokkary and Låg (1978) obtained their material from plough-layer soils. Miller and McFee (1983) obtained soils from mature oak woodlands. Their soils were higher in pH (pH5.8-7.3) than Hallen/Haw soils and they sampled only the surface 2.5cm of soil. Nevertheless, their results for exchangeable metals (1M $KNO_3$ extractable) suggested that the order of metal availability was:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Order : | Cd | > | Zn | > | Pb | > | Cu |
| % of total : | 23.2 | | 10.2 | | 7.5 | | 1.8 |

for sandy soils at or near neutrality

Other studies that have just assessed the amount of EDTA or $NH_4OAc$ extractable metals from smelter emission include those of Cartwright *et al.* (1976), Pedroli *et al.*(1990) and Scokart *et al.*(1983). Little evidence of metal movement existed in the study by Cartwright *et al.*(1976), although in one location on a cultivated soil the extractable Cd profile to 20cm depth showed an unusual distribution. The work by Pedroli *et al,*(1990) indicated that there was a remarkable proportion of Pb, that was extractable with EDTA at pH3.46, in the L and F layers of *Pinus sylvestris* afforested areas. However, in the mineral soil in the Ah/E part of the profiles, the proportions of extractable metals followed an order of availability:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Order : | Cd | > | Zn | > | Cu | = | Pb | sandy soils: |
| % of total : | 33 | | 16 | | 1.6 | | 1.5 | soil 1 |
| | 22 | | 17 | | 1.8 | | 1.2 | soil 2 |

Zn was still available as 7-15% of the total soil concentration even at depths of 2 to 4 metres. This is not so surprising when consideration is given to the highly acidic nature of the soils (mainly pH4.2 in $H_2O$ or less). Of particular interest is the study on heavy metal availability / mobility in soils polluted by aerial smelter emissions by Scokart *et al.* (1983). Using 1M $NH_4OAc$ extractions, they found that the mobility of the metals in the soil followed the order:

| | |
|---|---|
| Cd > Zn > Pb > Cu | for very acidic sandy soils |
| Cd > Zn > Pb, Cu | for neutral loamy soils |

In their study, two of the loamy profiles contained very high proportions of exchangeable metals due to their acidic profiles (pH4.7-5.7 at depths greater

than 10cm). Comparative results of Scokart *et al.* (1983) and this study are illustrated in Figs.3.6.10a,b and 3.6.11a,b. The high availability of the metals in the acidic sandy soil demonstrated the importance of factors such as pH and the % clay fraction of the soil. The neutral loamy soils had much less available metal although the availability of Cd was still quite high. In the Hallen soil, the low pH has enabled a high proportion of Cd and Zn to become available for movement despite the soil having a high clay fraction. However, the Haw soil was a higher pH, clay soil and hence the proportion of exchangeable ($\Sigma$ $\underline{WA}$ + $\underline{AN}$ + $\underline{Cc}$) Cd and Zn appears much reduced in relation to the three other soils. The mobility of heavy metals in Haw and Hallen Wood soil, in terms of % exchangeability, would appear to agree with the outcome of the study by Scokart *et al.*(1983) for sandy and loamy soils:

$Cd > Zn > Cu = Pb$ for Hallen Wood and Haw Wood clay soils

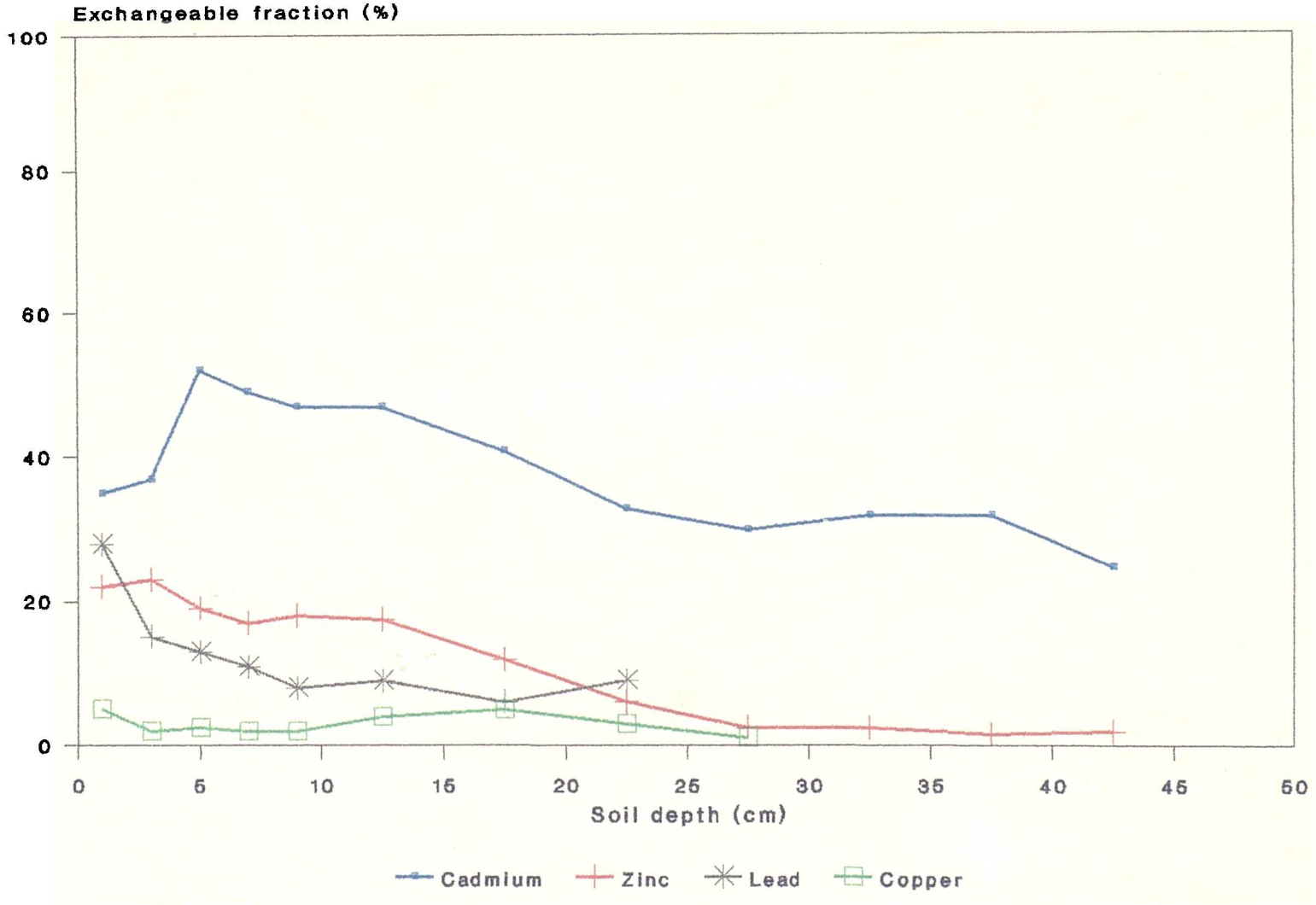



Fig.3.6.10a Exchangeable Fraction: Heavy Metals in Neutral Loamy Engis Soil (redrawn after Scokart et al. 1983)

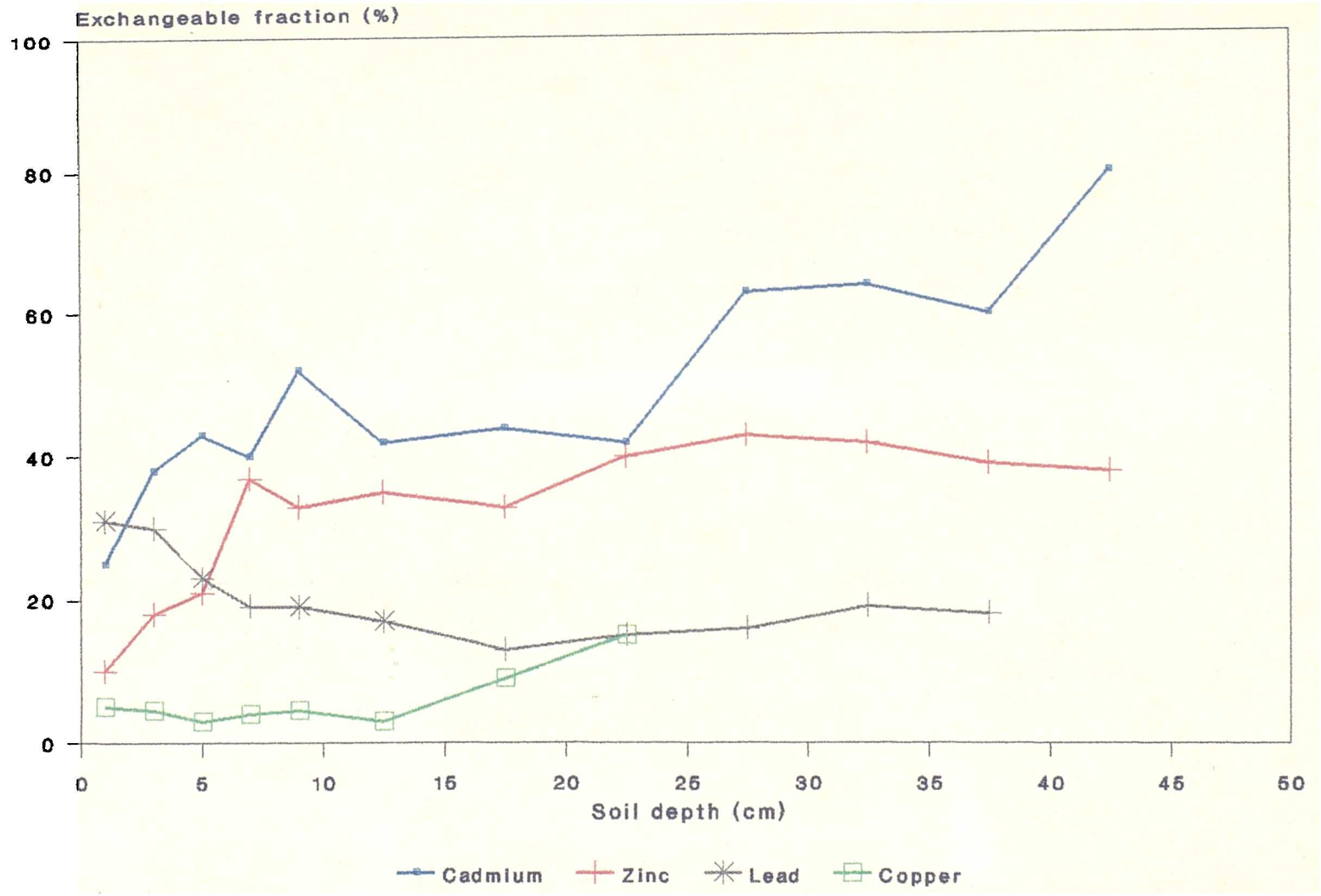



Fig.3.6.10b Exchangeable Fraction: Heavy Metals in Sandy Acidic Balen-Neet Soil (redrawn after Scokart et al. 1983)

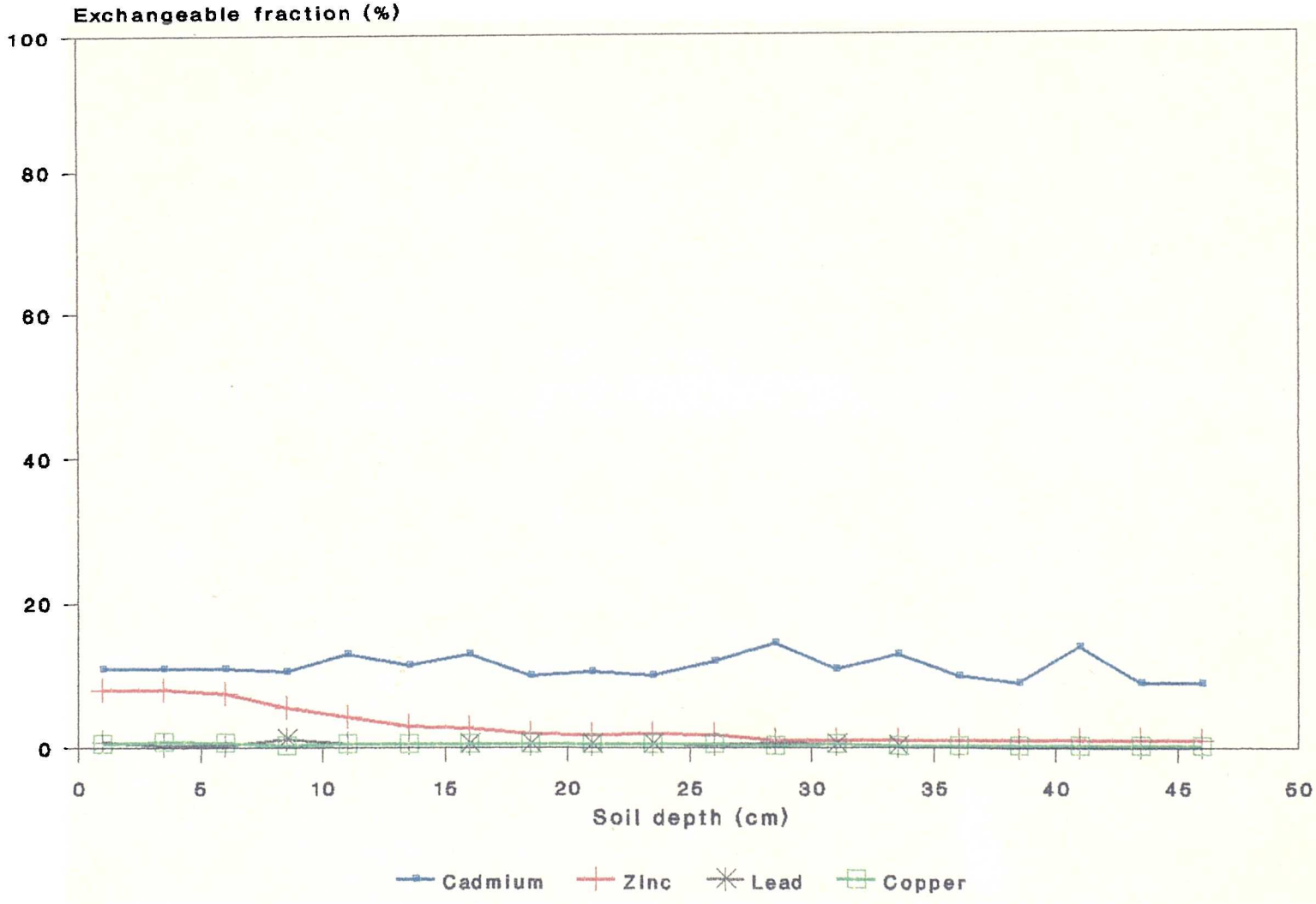



**Fig.3.6.11a Exchangeable Fraction: Heavy Metals in Clayey Weakly-Acidic/Neutral Haw Wood Soil (1987 Profile)**

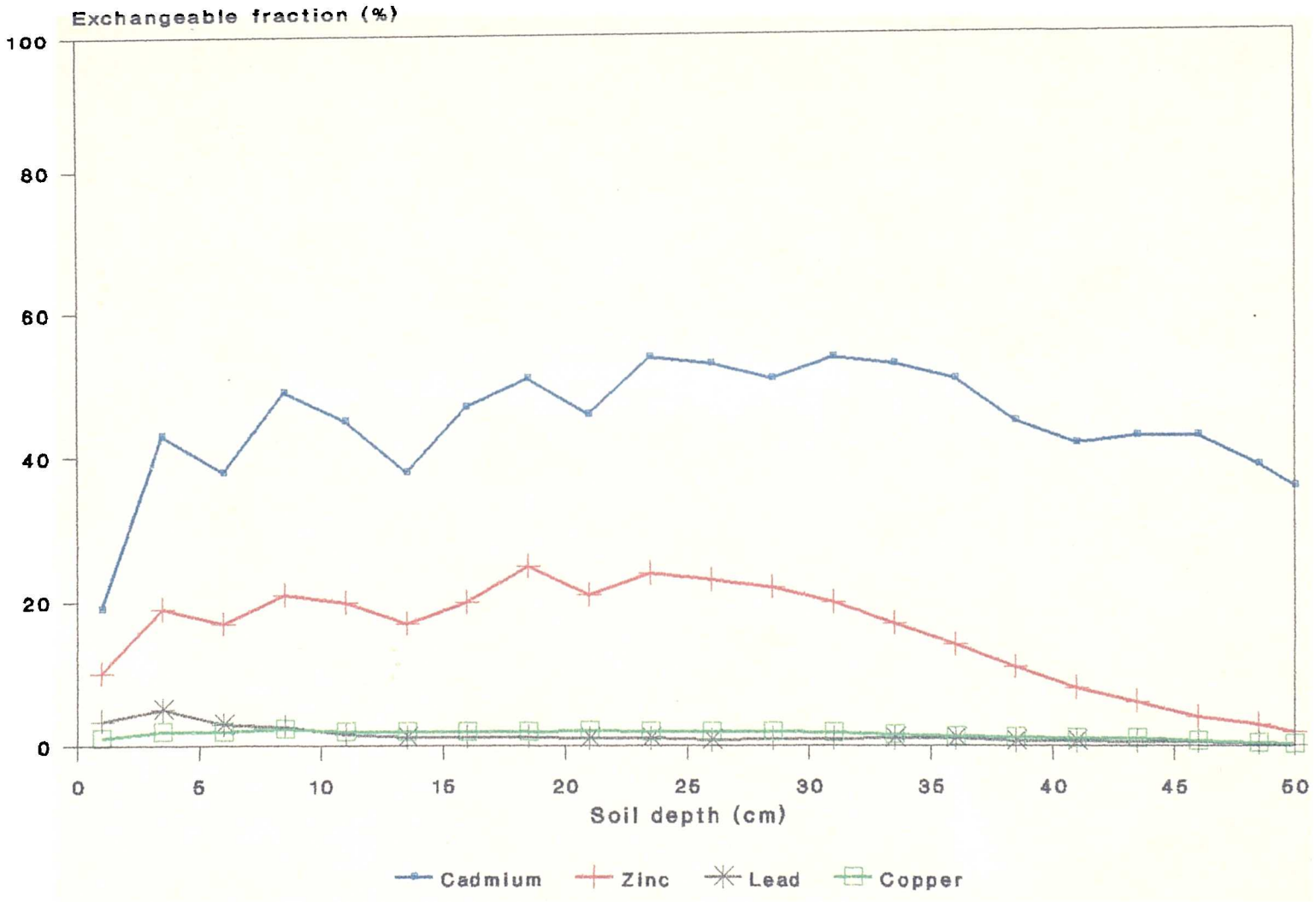



**Fig.3.6.11b Exchangeable Fraction: Heavy Metals in Clayey Acidic Hallen Wood Soil (1987 Profile)**

### 3. 6.8. Summary and Conclusions

(a) Chemical extraction techniques are commonly employed in the assessment of the bioavailability / mobility of heavy metals in soils and sediments. Despite their limitations, sequential extraction procedures are useful for assessing the relative importance of geochemical forms of heavy metals in soils.

(b) Haw and Hallen Wood soils were sequentially extracted so that Cd, Cu, Pb and Zn could be partitioned into operationally defined geochemical fractions. Neutral salts were used for determination of exchangeable heavy metals to ensure that the full effects of the soil pH were maintained.

(c) The residual (RES) fraction was the dominant individual fraction for all four heavy metals in both woodland soils. Greater than 90% of Cu and Pb were in the RES form in both soils. But Cd and Zn were much more available than Cu and Pb. All four metals have proportionally more non-residual (NRES) metal in the more acidified Hallen profile than in the Haw profile. Cd was the most available heavy metal with up to 71% of it's total metal concentration (MTOT) in an NRES form in Hallen Wood.

(d) The geochemical similarity that Cd and Zn are known to possess appears to have been expressed in both woodland soils. The similar proportionation of Cd and Zn in NRES forms (not including the residual fraction) and the greater quantitative abundance of zinc both help to explain how MTOT Zn distributions have changed in comparative unison with the MTOT Cd distributions with time (see Chapter 2, Section 3.3).

(e) The more mobile heavy metals, Cd and Zn, appeared to be associated with organic matter in Haw Wood mineral soil whereas in Hallen Wood pH and % base saturation seemed to be more closely associated with available Cd.

(f) EXCH K and EXCH, NRES, MTOT Mn appeared to be highly correlated with the distributions of available Cd, Cu, Pb and Zn. 2:1 clay minerals and Mn oxides might play an important role in in relation to heavy metal movement in Haw/Hallen soils.

(g) In comparison to Haw Wood soil, a reduced EXCH Ca, increased EXCH "acidic" cations (Al, Mn, Fe, Zn) and a much larger EXCH acidity existed in Hallen Wood soil. Such factors are likely to be contributory to any heavy metal movement down the Hallen profile.

(h) There appears to be a distinct dearth of literature with respect to the availability and potential mobility of heavy metals in soils contaminated aerially by industrial smelting works. The majority of literature deals principally with sandy soils where the physical nature of the soil may in itself be conducive to

encouraging some leaching of heavy metals. Certainly with respect to the detailed sampling procedure (soil taken every 2.5 cm depth), the nature of the soil (heavy clay soil) and the high levels of heavy metal contamination from aerial deposition, the study at Hallen and Haw Wood appears to be relatively unique. Only the study by Scokart et al.(1983) holds some comparison with regard to high levels of heavy metal contamination from aerial deposition. The evidence from this study would suggest that the bioavailabiliy / mobility of the heavy metals in Haw and Hallen soils decreased in the order:

$$Cd > Zn > Cu, Pb$$

# CHAPTER FOUR

# SOIL SOLUTION : HEAVY METAL SPECIATION

## 4.1. Introduction

The soil solution (labile aqueous phase) is a dynamic, open, natural water system whose properties represent the effects of soluble complex formation, oxidation-reduction, adsorption and precipitation-dissolution reactions that proceed concurrently; and hence the soil solution may be looked on as the principal seat of activity as a result of the action of biological, hydrological and geological agents in the soil (Sposito 1983). For ecological considerations the concentration and form of heavy metal species in the soil solution is of immense importance, because metal mobility and availability are closely related to the composition of the liquid phase (Brümmer 1986).

In the soil solution matrix heavy metals exist within a physical and chemical framework (physio-chemical speciation). An example of physical speciation is given in Fig.4.1.1. The dimensions given in Fig.4.1.1 are only tentative as the borderline between categories is difficult to establish because gradual transitions occur (Salbu 1987). The size distribution pattern for an element of interest will be influenced by the presence of other components / environmental factors that the water system possesses. However, the chemical speciation of a heavy metal may be defined as the distribution of the total concentration into various chemical forms; the most important factor in controlling the speciation of metals in soil solutions being the concentrations of various ligands (inorganic or organic) present and the stability of the resulting complexes (Bergkvist and Folkeson 1988, Bergkvist *et al.*1989). Again, it should be stressed that the prevalent ambient environmental conditions should also be taken into account and would affect the soil solution matrix.

Advances in the understanding of the environmental processes are presently hindered by the lack of suitable methods for the identification and quantification of chemical species and for the analysis of their behaviour in the environment (Bernhard *et al.*1986).

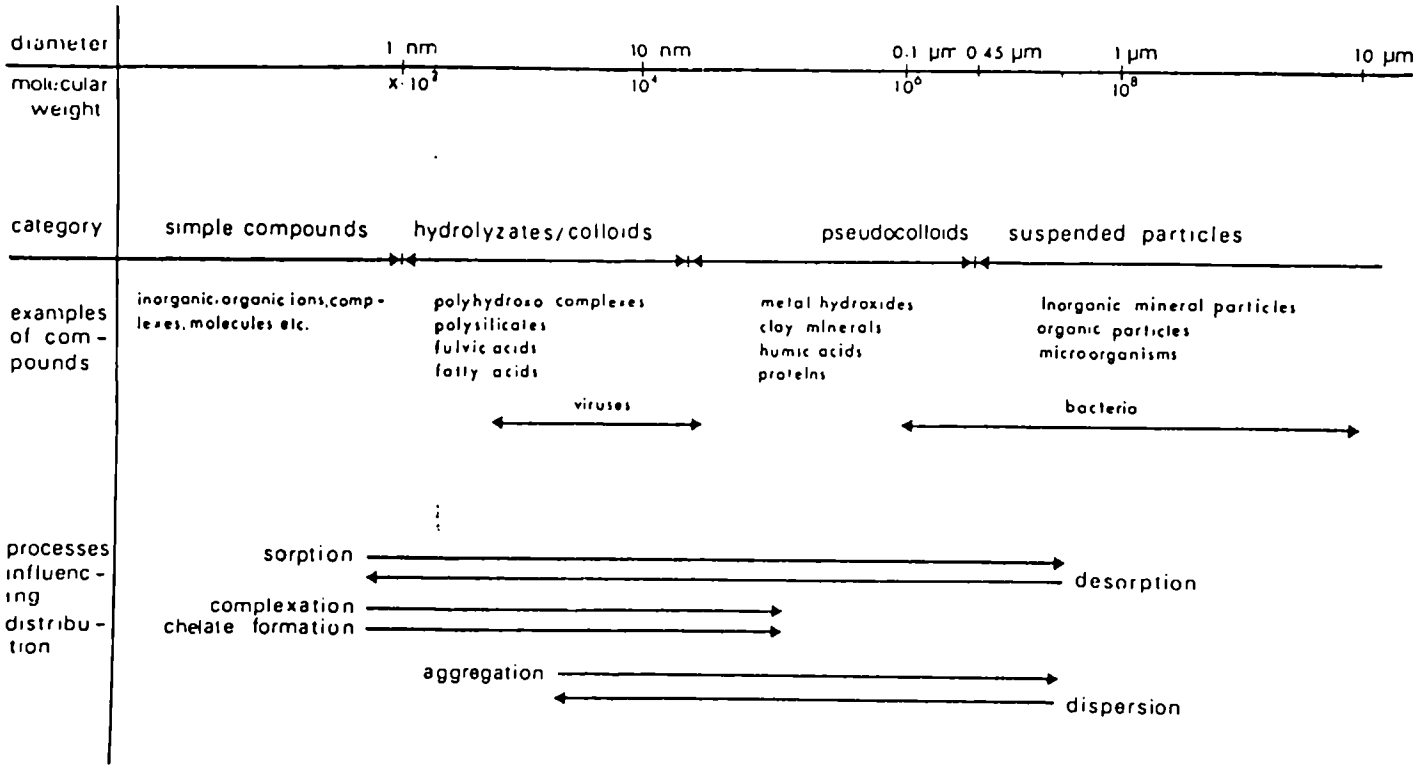



Fig.4.1.1 Association of trace elements with compounds in different size ranges. Transformation processes are indicated.

## 4.1.1. Chemical Speciation of Heavy Metals in the Soil Solution

There are numerous soil environmental factors to take account of when considering the chemical speciation of metals in soils (Fig.4.1.2 after Brümmer 1986). The soil solution is susceptible to change from its equilibrium or steady-state condition due to these environmental variables. Metals within the soil solution exist chemically either as free (uncomplexed) soil solution ions or as a range of complexes with both inorganic and organic ligands. Two types of soluble complexes are formed between metals and complexant ligands (Evans 1989):

(a) Outer sphere complexes - relatively weak electrostatic associations, hydrated cation/complexant ligand ion pairs.
(b) Inner sphere complexes - strong associations, covalently linked metal/complexant ligand.

Both of the above complex forms can be either negatively or positively charged or be electrically neutral. The formation constant is a measure of the strength of the association between a metal and a complexant ligand. Also, a free ion $M^{n+}$ in the liquid phase of the soil will precipitate when the solubility product of its compound with any reaction partner $R^{m-}$ is reached (Cottenie 1980). The two major mechanisms that are involved in the retention of metals by soil are (Evans 1989):

(a) Adsorption reactions - outer sphere/inner sphere complexes with the surfaces of mineral and organic constituents.
(b) Precipitation reactions - formation of new secondary mineral phases.

Non-specifically absorbed ions are dependent only on the relative charges of the metal species in solution and that of the charged surface. However, for specifically adsorbed ions the extent of adsorption depends on the intrinsic formation constant of the metal-surface complex and of the pH of the soil solution.

Metal ions generally behave as Lewis acids, because they have vacant orbitals which can accept electrons, whereas ligands behave as Lewis bases because they have the capacity to donate electrons. The metal cations can be classified as (see Fig.4.1.3 after Jørgensen and Jensen 1984, Morgan 1987, Sposito 1981):

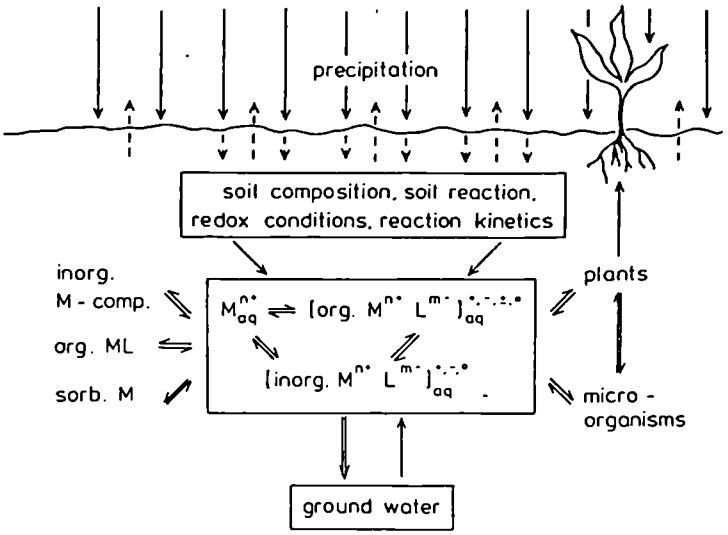



Fig.4.1.2 Schematic presentation of heavy metal reactions in soils. Relationship between solid metal phases [inorganic metal compounds, organic metal compounds (org. ML), sorbed metals], soluble metal species (metal ions, organic and inorganic metal complexes), metal uptake by plants and microorganisms, and metal transfer from decomposing plants and microorganisms to the soil solution

Fig.4.1.3 A catalog of hard and soft Lewis acids and bases in soil solutions

*LEWIS ACIDS*

*Hard Acids*

$H^+$, $Li^+$, $Na^+$, $K^+$, ($Rb^+$, $Cs^+$), $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, ($Ba^{2+}$), $Ti^{4+}$, $Zr^{4+}$, $Cr^{3+}$, $Cr^{6+}$, $MoO^{3+}$, $Mn^{2+}$, $Mn^{7+}$, $Fe^{3+}$, $Co^{3+}$, $Al^{3+}$, $Si^{4+}$, $CO_2$

*Borderline Acids*

$Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, ($Pb^{2+}$)

*Soft Acids*

$Cu^+$, $Ag^+$, $Au^+$, $Cd^{2+}$, $Hg^+$, $Hg^{2+}$, $Ch_3Hg^+$; pi-acceptors such as quinones; bulk metals

*LEWIS BASES*

*Hard Bases*

$NH_3$, $RNH_2$, $H_2O$, $OH^-$, $O^{2-}$, ROH, $CH_3COO^-$, $CO_3^{2-}$, $NO_3^-$, $PO_4^{3-}$, $SO_4^{2-}$, $F^-$

*Borderline Bases*

$C_6H_5NH_2$, $C_5H_5N$, $N_2$, $NO_2^-$, $SO_3^{2-}$, $Br^-$, ($Cl^-$)

*Soft Bases*

$C_2H_4$, $C_6H_6$, $R_3P$, $(RO)_3P$, $R_3As$, $R_2S$, RSH, $S_2O_3^-$, $S^{2-}$, $I^-$

R = organic molecular unit. ( ) indicates a tendency to softness.

(a) "Hard" metal cations - small ionic radius, high charge, do not contain unshared pair of valence electrons ("noble gas structure"), retain their valence electrons very strongly e.g. $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $Al^{3+}$. Metals such as $Mn^{2+}$ are practically "borderline" metal category (c).

(b) "Soft" metal cations - large ionic radius, small charge, unshared pairs of valence electrons eg. $Cu^{+}$, $Cd^{2+}$.

(c) "Borderline" metal cations - eg. $Zn^{2+}$, $Cu^{2+}$. These fall into neither category (a) or (b). Some metals, such as $Fe^{2+}$, fall closer to the "hard" metal category (a) than does $Pb^{2+}$ which is more affiliated to the "soft" metal category (b).

Soft metal cations (e.g. $Cu^{+}$) form stronger complexes with heavier electron donors from the 3rd, 4th and 5th rows of the periodic table, whereas hard metal cations (eg. $Mg^{2+}$) form their strongest complexes with the electron donors of the 2nd row so that the overall donor preference is (Morgan 1987):

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (a) | F | > | O | > | N | ≈ | Cl | > | Br | > | I | > | S (for "hard" metal cations) |
| (b) | I | > | Br | > | Cl | » | F | ⎫ | | | | | |
| (c) | | | As | > | S | » | O | ⎬ | (for "soft" metal cations) | | | | |
| (d) | | | As | > | P | » | N | ⎭ | | | | | |

Essentially, the "hardness" and "softness" properties for Lewis acids and bases for many kinds of systems follow two HSAB (hard and soft acid-base) rules (Pearson 1968):

(a) Equilibrium - hard acids prefer to associate with hard bases, soft acids with soft bases.

(b) Kinetics - hard acids react readily with hard bases, soft acids with soft bases.

Despite this, "softer" metals will still form aqueous complexes, solid phases and adsorbed species with "hard" donors. The "softer" metals have a preference for softer ligands, but every Lewis acid-base affinity has both an entropic and enthalpic component. Hence for a "hard" donor, such as $OH^{-}$, there is an appreciable entropic component with most metal bonding. In the case of "soft" metals, this usually includes a dominant enthalpic term. Therefore, interestingly, the affinity series of $O^{-}$ donor aqueous $MOH^{+}$ complexes of the bivalent metals is (Morgan 1987):

Hg > Pb > Cu > Fe > Co > Zn > Mn > Cd > Mg > Ca

In environmental terms, industrial pollution from base metal smelting activities can therefore potentially introduce excessive quantities of Lewis acid metals into ecosystems. The biological implication of this will depend on the quantity and quality of Lewis bases, and numerous environmental aspects including pH which will all influence the resulting chemical speciation of the metals in a soil system.

### 4.1.2. The Quality: Form of Heavy Metals Cd, Cu, Pb and Zn in Soil Solutions

Cd, Cu, Pb and Zn exist in various chemical and physical forms within the soil solution. These forms and the environmental conditions that determine the distribution of the metals in the different forms of aqueous solutions are (Rohbock 1986; see also Florence and Batley 1980):

| Metal Form | Principal Environmental Parameters |
|---|---|
| 1. Free metal cations e.g $Pb^{2+}$ | 1. pH value |
| 2. Inorganic complexes e.g. $CdCl^{+}$ | 2. Redox conditions |
| 3. Organo-metal complexes e.g. $(CH_3)_4Pb$ | 3. Temperature |
| 4. Organic complexes, chelates | 4. Concentration of complexing agents |
| 5. Metal species bound on high molecular organic materials e.g. metal lipids | 5. Particle size |
| 6. Metal species in form of dispersed colloids | 6. Time of dissolution |
| 7. Metals adsorbed on colloids | 7. Concentration of adsorbing material |
| 8. Large particles of insoluble material, silicates | 8. Mass concentration of the metals in the solution |

Metal forms 1-4 are generally considered to be the metal species in the soluble fraction of the aqueous phase (Guy and Chakrabarti 1975).

In relation to the total concentration of certain metals in solution, there has been increasing environmental concern over particular soluble species of these metals (Jørgensen and Jensen 1984, Sibley and Morgan 1975). The metal forms in solution may not all be equally available to plants and aquatic organisms, and hence the importance of partitioning the concentrations of trace

metals in solution into charged and neutral chemical species (Allen *et al.*1980, Florence and Batley 1980). For example, the metal-protein interaction, leading to carrier-mediated transport of the metal across the membrane of a fish gill will, for divalent metals, usually be thermodynamically favoured when the metal is in the simplest chemical form e.g. $Cu(H_2O)_4^{2+}$, $CuCl^+$, or $Cu(OH)^+$ (Florence and Batley 1981).

The most important inorganic ligands for heavy metal complexation in the soil solution are $Cl^-$ and $SO_4^{2-}$ (Bergkvist and Folkeson 1988, Bergkvist *et al.* 1989). Inorganic anions can increase the concentration of metals in solution by forming soluble inorganic metal complexes (Brümmer 1986). For example, the importance of chlorine increasing the concentrations of cadmium in solution (Bingham *et al.*1983, Garcia-Miragaya and Page 1976, Gerth *et al.*1981, Hahne and Kroontje 1973) and its mobility through the soil (Doner 1978) is a matter for concern. For instance the chloro-complex, $CdCl^+$, appeared to be affiliated with cadmium corn shoot uptake rather than the free ion, $Cd^{2+}$ (Sposito and Bingham 1981). But from the evidence available, Bingham *et al.*(1984) suggest that the principal bioavailable form of Cu, Zn and Cd is the bivalent free metal cation. In proportional terms (from data collected by Cronan 1980, Bourg and Védy 1986 and Nilsson and Bergkvist 1983) Bergkvist *et al.*(1989) suggested that the free hydrated metal is the dominant inorganic species form in the soil solution.

The other group of anions that are important in metal speciation are the organo-anions. Dissolved organic carbon concentrations in soil waters are commonly much higher than those in rivers and lakes, and organic complexation plays an important part in the chemistry of some trace elements in some waters; but such complexation is difficult to evaluate quantitatively because of our lack of knowledge of humic substances (Drever 1982). It has been estimated that between 70-80% of the organic matter in most inorganic soil consists of humic materials (humic and fulvic acids) (Schnitzer 1980). Fulvic acids, which form soluble metal chelates over a wide pH range, can potentially increase the solubility of heavy metals favouring their mobility, whereas humic acids form much more stable metal complexes, but are generally much less soluble than fulvates especially in an acid medium (Cottenie 1980). Since the donor atoms in most organic complexes are oxygen atoms, metals that readily form hydroxo-complexes in water can be expected to form relatively strong complexes with organic ligands (Evans 1989). Humic and fulvic acids are high molecular weight and more structurally complex organic ligands, whilst more simplistic ligands include citric, oxalic, acetic etc. acids. Ligands such as

**Table 4.1.1 % Total Cadmium Speciation for a Nitrilotriacetate (NTA) system as a function of pH (after Elliott and Denneny 1982)**

Total NTA ligand concentration = $5.4 \times 10^{-6}$M

| Species | pH4 | pH5 | pH6 | pH7 | pH8 |
|---|---|---|---|---|---|
| $Cd^{2+}$ | 89.3 | 64.7 | 49.5 | 46.4 | 45.7 |
| $CdNTA^-$ | 10.7 | 35.2 | 50.5 | 53.6 | 54.0 |

---

fulvates range in diversity e.g. phthalate sites are considered to be the most important binding site for metals in relation to acetylacetonate and salicylate binding sites (Murray and Linder 1984, Linder and Murray 1987); and there are also distinct differences between the form and nature of different fulvates (Sposito *et al.*1982b).

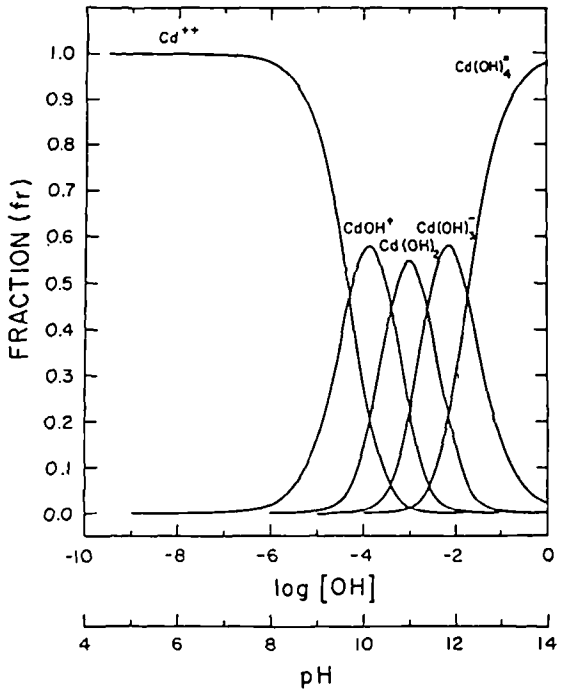
Evans (1989) suggested that the extent of metal complexation depended not only on the relative amounts of metal and complexant ligands, but also on the pH of the water. The effect of pH was illustrated by Hahne and Kroontje (1973) in the hydrolysis of Cd, Pb and Zn (Fig.4.1.4). The effect that pH can have on organic complexation is shown in Table 4.1.1.

In terms of soil acidification, changes in metal speciation can be anticipated as a result of a decrease in pH; the degree to which a particular metal is affected will depend on the acid-base properties of the ligand and the soil surfaces, and on the stability of the various metal-ligand and metal solid surface species (Campbell *et al.*1983). An idea of the principal chemical species of metals found in oxic soil solutions is given in Table 4.1.2 (after Sposito 1983, Sposito and Page 1984). The importance of free metal cations and sulphate complexes in acid soils is noteworthy (Sposito 1983).

## 4.1.3. Quantity: Concentrations of Heavy Metals in Soil Solutions

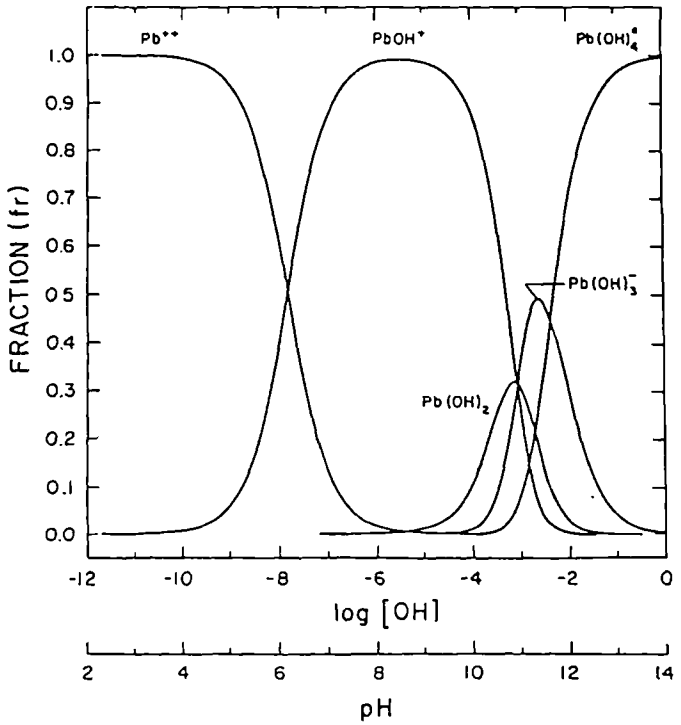
The total amounts of the individual heavy metals in solution are usually very low (Jones and Jarvis 1981). The solubility behaviour of heavy metals determines mobility, leaching, availability and toxicity of these elements in soils (Brümmer and Herms 1983). Therefore, the increased solubility of heavy metals with decreasing pH due to the formation of metal aqua ions has great

Fig.4.1.4a



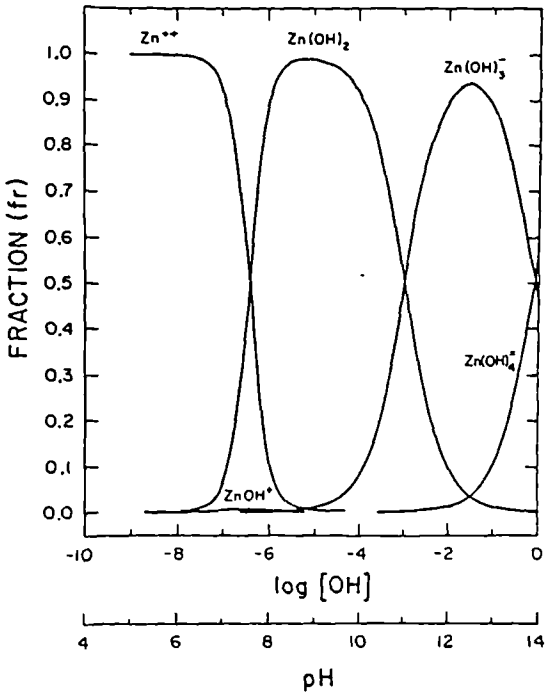

Distribution of molecular and ionic species of divalent Cd at different pH values.

Fig.4.1.4b




Distribution of molecular and ionic species of divalent Pb at different pH values.

Fig.4.1.4c




Distribution of molecular and ionic species of divalent Zn at different pH values.

## Table 4.1.2 Principal Chemical Species of Cd, Cu, Pb, and Zn in Oxic Soil Solutions

| Metal | Principal Species: Acid Soils | Principal Species: Alkaline Soils |
|---|---|---|
| Cd | $Cd^{2+}$, $CdSO_4^o$, $CdCl^+$ | $Cd^{2+}$, $CdCl^+$, $CdSO_4^o$, $CdHCO_3^+$ |
| Cu | $Org^a$, $Cu^{2+}$ | $CuCO_3^o$, $Org^a$, $CuB(OH)_4^+$, $Cu(B(OH)_4)_2^o$ |
| Pb | $Pb^{2+}$, $Org^a$, $PbSO_4^o$, $PbHCO_3^+$ | $PbCO_3^o$, $PbHCO_3^+$, $Pb(CO_3)_2^{2-}$, $PbOH^+$ |
| Zn | $Zn^{2+}$, $ZnSO_4^o$ | $ZnHCO_3^+$, $ZnCO_3^o$, $Zn^{2+}$, $ZnSO_4^o$, $ZnB(OH)_4^+$ |

a : Organic complexes eg. fulvic acid complexes.

Order of species from left to right is roughly that of decreasing concentration.

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environmental interest (Jørgensen and Jensen 1984). With respect to plant uptake, a knowledge of the concentration and form of a trace element in the soil solution and the factors that control these is essential (Sanders 1982).

Soil pH change as a result of the increase in soil acidification over time, or more especially as a result of acid precipitation should potentially increase heavy metal concentrations in soil solutions (Bergkvist 1987, Bergkvist and Folkeson 1988, Bergkvist *et al.* 1989, Tyler *et al.* 1987). Certainly the leaching and mobility of such metals are affected by acidification processes (Campbell *et al.* 1983, Straughan *et al.* 1981). The pH dependence of the solution concentration of Cd, Cu, Pb and Zn shows that the mobility and availability of the heavy metals is high at strongly to extremely acidic soil reactions; and therefore, a high input of these metals, especially in strongly acidic forest soils, may lead to toxic environmental effects due to accumulation of the elements (Brümmer 1986).

However, metal ion concentrations in solution will be controlled at equilibrium by the solid phase that results in the lowest value of the activity of the metallic ions in solution (Sposito 1981). Therefore the overall effect of pH on the concentration of metals in the soil solution will be affected by the constituents that make up the soil. This was effectively illustrated by Brümmer and Herms (1983) and Herms and Brümmer (1984) for different levels of

organic matter in the soil. Organic matter possesses a much higher binding capacity for heavy metals at strongly acidic soil reaction than do mineral substances (Brümmer and Herms 1983, Herms and Brümmer 1984, Tiller *et al.* 1984). The effect of organic matter over a range of pH in the adsorption of heavy metals in relation to clay minerals was illustrated by Bourg (1981) (Fig.4.1.5a - data compiled from Farrah and Pickering 1976a, 1976b, 1976c, 1977, Hatton and Pickering 1980). The effect of different clay contents and different total heavy metal contents is shown in Fig.4.1.5b (from Brümmer and Herms 1983).

Since solubility, ionic status and adsorption strength of most heavy metals depend upon the pH and type of organic / mineral solid phase present at the vegetation surface and in the soil, a strong interaction between deposited trace elements and other atmospheric pollutants (acids, organic compounds, mineral particles) can be expected (Ottar *et al.*1989). Therefore, as well as the soil constituents the amount of Lewis anion bases can also determine the concentration of soluble heavy metals in the soil solution. Wiklander (1976, 1980) suggested that the solubility and retention of cations in soils can be affiliated to the kind of anions in association with them. The effectiveness of anions in encouraging adsorption and decreasing the leaching of the cations was:

$$HPO_4^{2-} > H_2PO_4^{-} > SO_4^{2-} > NO_3^{-} \approx Cl^{-}$$

The influence of anion production and mobility as a consequence of acid precipitation can also affect nutrient leaching (Cole and Johnson 1977, Cronan *et al.*1978). Based on the concept of Nye and Greenland in 1960 leaching cannot occur without an anion or anions to maintain electrochemical neutrality in soil solution, cation exchange reactions not withstanding (Johnson and Cole 1980). The anion required for leaching of a cation appears in the soil solution as a proton acid and will aid to drive acidification (Ulrich and Matzner 1986). A polyvalent anion such as sulphate is much more specifically bound by hydrated oxides of Al and Fe (and other minerals), creating free sites to adsorb cations (Wiklander 1976) than are other ions such as nitrate and chloride. Thus sulphate adsorption can lead to base cation retention, but when sulphate saturation is reached leaching of both sulphate and associated base cations occurs - see Fig.4.1.6 (after Cresser *et al.*1988).

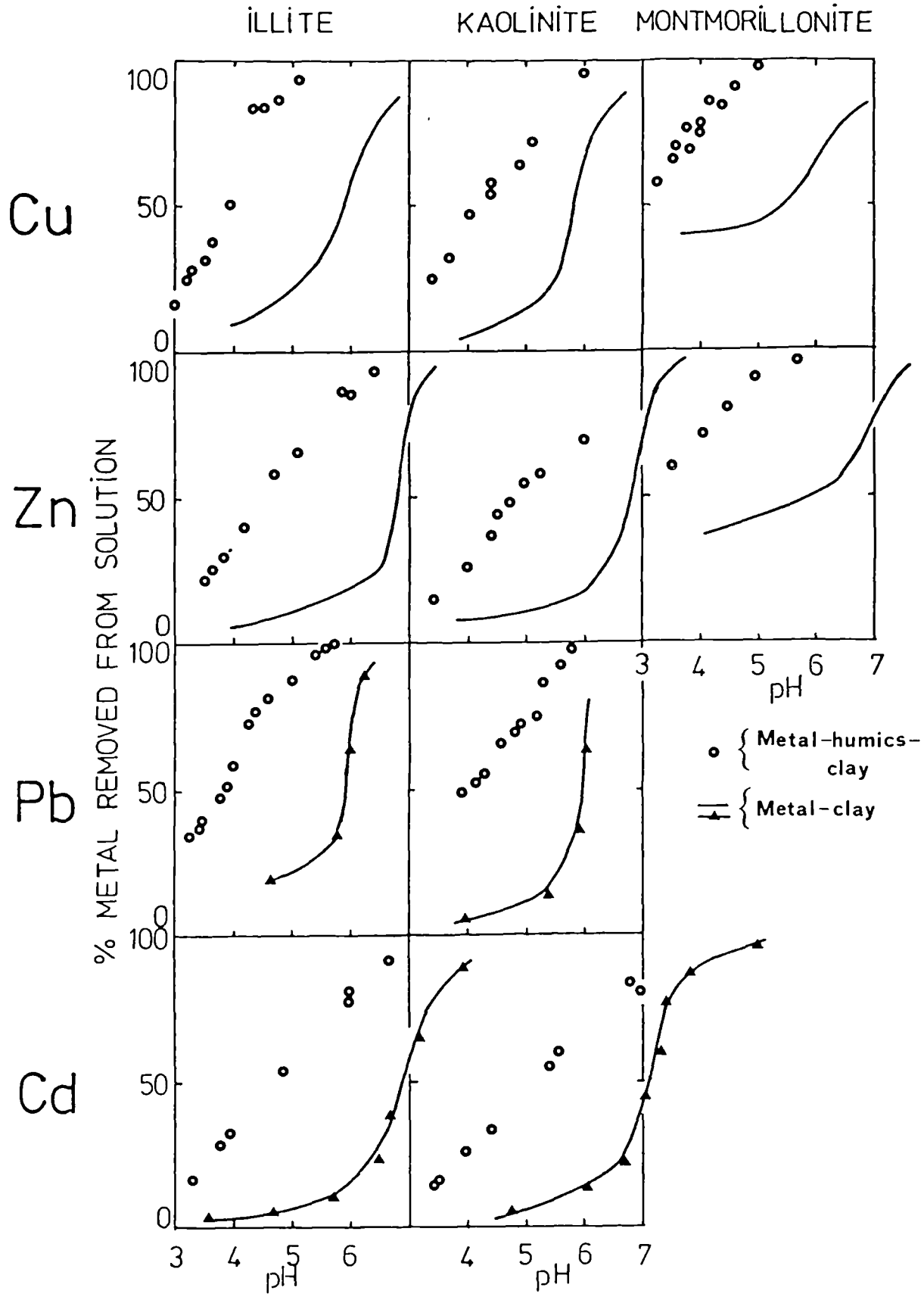


Fig.4.1.5a Adsorption of trace metals on clays in the presence and in the absence of particulate humic acid

RELATION BETWEEN TOTAL CONTENT AND SOLUTION CONCENTRATION OF HEAVY METALS

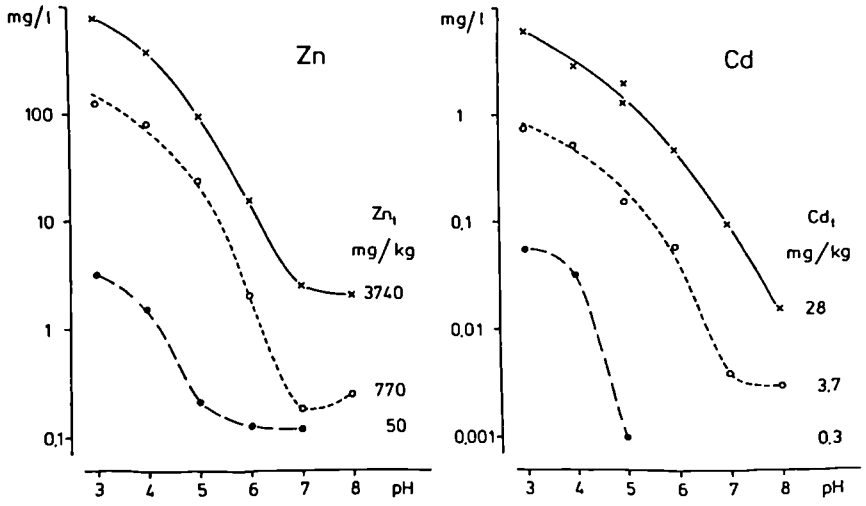


Fig.4.1.5b Concentration of Zn and Cd in equilibrium solutions of three soil samples (A horizons) with different total content of these elements in relation to pH.

EFFECT OF DIFFERENT CLAY CONTENTS

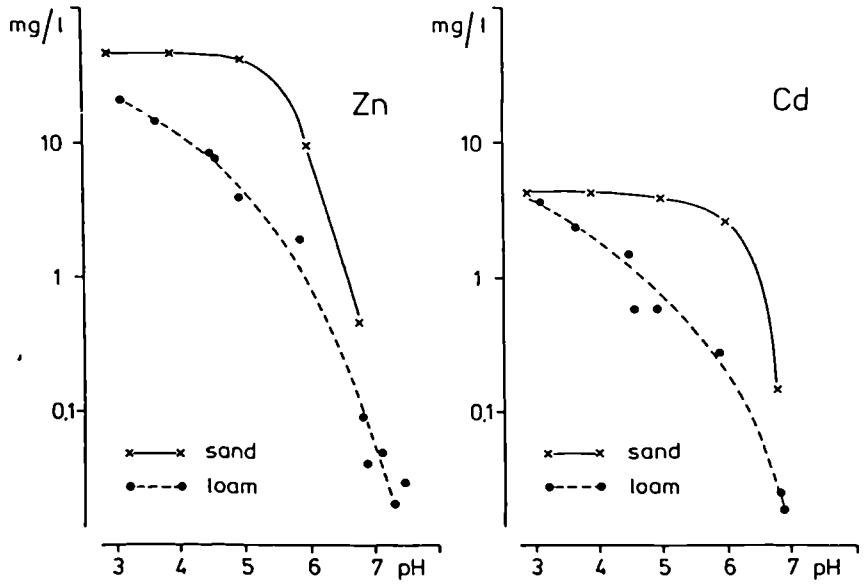


Fig.4.1.5b Zn and Cd concentrations in equilibrium solutions of sandy and loamy subsoil samples of comparable total Zn and Cd content

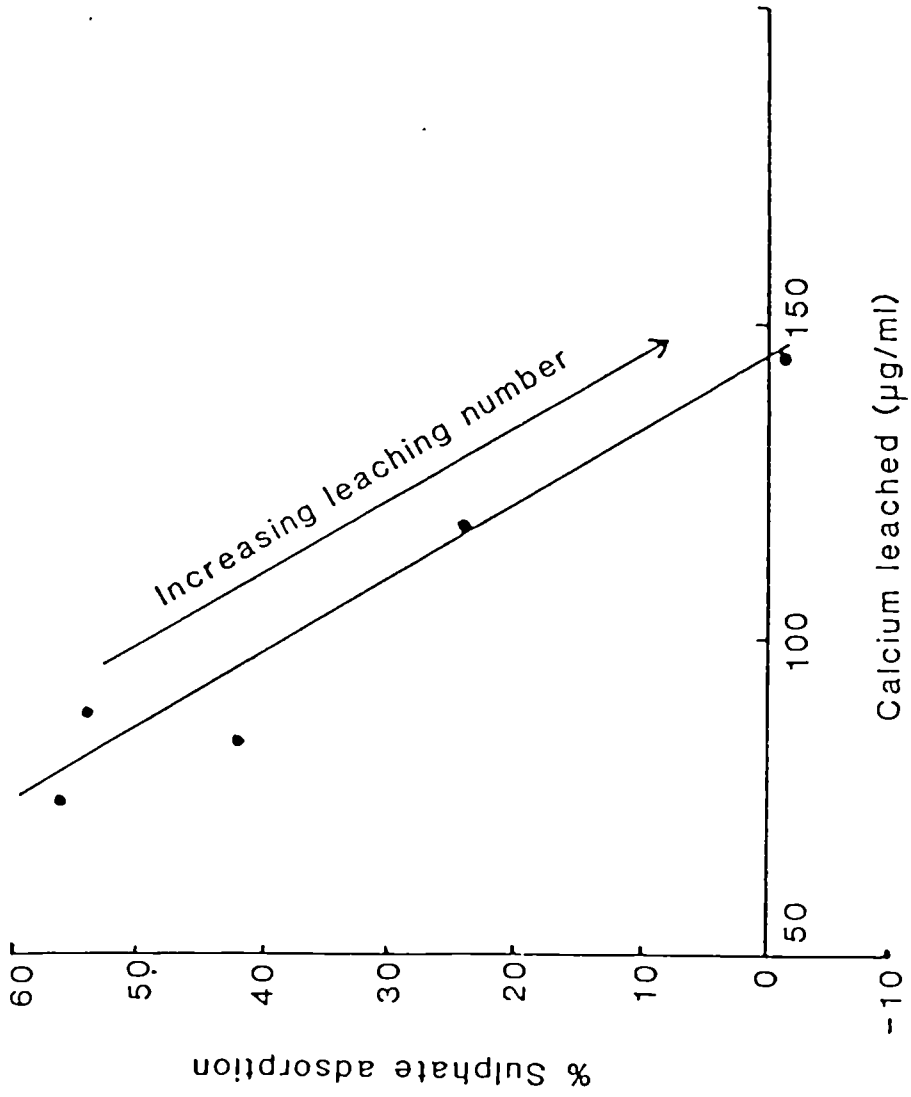


Fig.4.1.6 Leaching of calcium from a reconstituted podzol profile over five simulated acid rain storms (pH 3.5) as a function of declining sulphate adsorption.

## 4.2. Chemical Composition of the Soil Solution

### 4.2.1. Extraction of the Soil Solution

The problem of obtaining the "true" soil solution has not yet been solved, but several preferred methods of extracting aqueous phases from soil have been developed in the context of a compromise between chemical accuracy and analytical convenience (Sposito and Page 1984). Essentially, the soil solution is an operationally defined medium. The principal methods used to extract the soil solution include:

(a) Displacement by immiscible fluid (including b, c or d).
(b) Displacement by suction (vacuum).
(c) Displacement by pressure.
(d) Displacement by centrifugation.

A successful column-displacement method was developed as early as the 1920's (Parker 1921). A centrifuge method was developed much later in the 1960's (Davies and Davies 1963). Numerous variations on the theme of technique have been explored (e.g. Adams 1971, Benians *et al.* 1977, Kinniburgh and Miles 1983, Larsen and Widdowson 1968, Murbarak and Olsen 1976). It is also possible for different techniques to obtain similar ionic compositions of soil solutions from the same soils (Adams *et al.*1980).

There are a number of problems associated with such procedures (some of which were discussed in Chapter 3 Section 5). Some of these problems include:

(a) Interferences caused by the filter - principally from adsorption-desorption reactions with dissolved constituents as the extracted solution passes through (Sposito and Page 1984).
(b) Volume of water: soil ratio - a soil sample that has been saturated with water prior to extraction may differ considerably in its composition from that of the "true" soil solution at ambient water contents (Sposito and Page 1984). But the volume of soil solution needed for chemical analysis varies with the ionic components to be determined, their ionic concentration, and the analytical methods that are employed (Adams *et al.* 1980).
(c) Period over which soil and water attain equilibrium - there is a suggestion that soil solutions may take a number of days to attain equilibrium (Larsen

and Widdowson 1968, Moss 1963), although the longer soil is maintained in a re-wetted state, the greater the risk of processes such as ammonification (Larsen and Widdowson 1968).

Despite the drawbacks, the soil solution composition data, which provide the total concentrations of dissolved (i.e. filterable under designated conditions) constituents, make up the primary information requisite to the description of the soil solutions at known temperature and pressure according to chemical thermodynamics and kinetics (Sposito and Page 1984).

### 4.2.2. Assessment of Heavy Metal Aqueous Species

There are a wide range of different techniques used to asses the chemical speciation of metals such as Cd, Cu, Pb and Zn in natural waters. The solution containing the metals can be separated into different physical component sizes (Harrison 1987, Salbu 1987). In practice, the first step applied in the separation of particulate from "soluble metals" involves filtration through a 0.45 μm pore size membrane filter (Förstner and Wittmann 1979, Mattigod and Page 1983). Essentially this physical separation provides the isolation of metal forms 1-4 in Rohbock's scheme (see Section 4.1.2). Such schemes are perhaps somewhat simplistic as, for example, trace metals that are adsorbed on colloidal oxide particles of diameters less than 0.45μm will also be classified as soluble species (Sposito 1983, Mattigod and Page 1983).

In the 1985 Athens conference on heavy metals, Cu, Pb, Cd and Zn were found to be most frequently subject to speciation procedures (including chemical extraction techniques) (Reuther 1987). Some of the analytical techniques used in assessing metal complexes in solution are listed in Table 4.2.1. Such techniques have been reviewed by Campbell and Tessier (1987), Florence and Batley (1980), Morrison (1987) and Saar and Weber (1982). Salbu (1987) and Florence and Batley (1977) reported requirements that should be met by fractionation techniques for speciation purposes:

(a) Fractionation *in situ* or at the site is essential as storage effects are then avoided.
(b) Rapid fractionation - avoids the establishment of equilibria between species retained and to be separated during the fractionation (i.e. the production of species of interest during fractionation).

## Table 4.2.1 Some Techniques used in Assessing Metal Complexes in Solution and Natural Waters

| | Technique | Reference Examples |
|---|---|---|
| 1. | Electron spin resonance spectroscopy (ESR)<br>Electron paramagnetic resonance spectroscopy (EPR) | Boyd *et al.*(1981)<br>Saar & Weber (1982) |
| 2. | Ion-selective electrode potentiometry | Saar & Weber (1980)<br>Frazer *et al.*(1983) |
| 3. | Spectrofluorometry | Ryan & Weber (1982 a, b)<br>Blaser & Sposito (1987) |
| 4. | Anodic stripping voltammetry (DPASV) | Figura & McDuffie (1979, 1980)<br>Florence & Batley (1977) |
| 5. | Ultra-violet irradiation | Florence & Batley (1977)<br>Laxen & Harrison (1981) |
| 6. | Solvent extraction | Florence & Batley (1981) |
| 7. | Dialysis | Borg (1987) |
| 8. | Ultrafiltration | Laxen & Harrison (1981) |
| 9. | Ozonolysis | Laxen & Harrison (1981) |
| 10. | Ion-exchange resins | Florence & Batley (1977)<br>Camerlynck & Kiekens (1982) |
| 11. | Gel filtration chromatography | Gregson & Alloway (1984)<br>Gerritse & Salomons (1983) |

Other techniques include :

(a) Radiotracers
(b) Filtration
(c) Centrifugation
(d) Electrophoresis

(c) Equipment surface area to sample volume ratio should be small in order to reduce sorption. However, conditioning with a sample aliquot minimizes this effect.

(d) The method should not be sensitive to clogging.

(e) Stability of colloids should not be disturbed (e.g. aggregation).

(f) Aggregates present should not be disrupted by stirring of solutions.

(g) No reagents should be added.

(h) The contamination risk should be kept low (e.g. closed systems).

(i) Techniques providing large volume fractions are favourable as:

(1) The determination limits of elements can be lowered by concentrating the samples from larger volumes.

(2) Further investigations (e.g. different analytical methods, biotests) can be performed.

(j) Avoidance of adsorbed and solid trace metal species in water samples.

(k) Preservation of the sample before analysis.

(l) Sensitivity (mmol $m^{-3}$ or better) in the case of water samples.

Since no technique is available for unequivocal characterisation of any specific metal form at the concentrations normally encountered in natural waters and the metal species analytically obtained may not reflect the true chemical speciation in the original water sample in all cases, it must be realised that any such speciation schemes are "operationally defined" (see Chapter 3 Section 5) (Florence and Batley 1980, Harrison 1987). For example, in the use of Chelex-100 resin, "free metal ion" has to be interpreted to include any complex whose trace metal component can be extracted by the oxygen and nitrogen-containing ligands on the resin (Sposito 1983).

### 4.2.3. Ion-Exchange and Other Techniques used for Metal Speciation in Soil Solutions

Ion-exchange has been employed in this thesis: ion-exchange techniques are simple, inexpensive and, with care, present little opportunity for sample contamination (Campbell and Tessier 1987). Against this, however, Salbu (1987) suggested that:

(a) Ionic exchange / chelating resin separation can essentially be slow and distortion of the original distribution patterns may occur - flow rates are therefore important.
(b) The column may also act as a gel-filtration resin while filtration through an ion-exchange membrane may be affected by clogging.

Despite any drawbacks, ion-exchange techniques appear to be used frequently (Reuther 1987) and have proved very useful in evaluating metal speciation in aqueous systems (Campbell and Tessier 1987). Its application in heavy metal speciation of Cd, Cu, Pb and Zn in soil solution is shown in Table 4.2.2.

Amberlite resins appear to be quite frequently used in such studies. After the pioneering work of Batley and Florence, Chelex-100 resin has found much use in the speciation of metals in natural waters (e.g. Figura and McDuffie 1979, 1980, Florence 1977, Florence and Batley 1977, Lee *et al.*1976).

Other techniques that have been used to assess Cd, Cu, Pb and Zn speciation in the soil solution are shown below (most of the examples again relating to soil solution studies):

(a) Dialysis - Bergkvist *et al.*(1989), Cox *et al.*(1984), Minnich and McBride (1987).
(b) Gel filtration chromatography - Baham *et al.*(1978), Butterworth and Alloway (1981), Gerritse and Salomons (1983), Gregson and Alloway (1984), Sposito *et al.*(1976).
(c) Solvent extraction - Hodgson *et al.*(1965).
(d) Ion-selective electrodes - Cavallaro and McBride (1980), McLaren *et al.* (1981), Minnich and McBride (1987), Sanders (1982), Sanders and Bloomfield (1980).

These methods, as with all metal speciation techniques, tend to have their own forms of inherent problems (Harrison 1987, Morrison 1987, Salbu 1987); but full understanding of chemical transitions will come about only through improved knowledge of metal speciation which is complemented by the analytical studies of real water samples (Harrison 1987).

**Table 4.2.2 Examples of Metal Speciation Studies Using the Method of Ion-Exchange Resins (Principally in soil solutions and related waters)**

| | Elements | Resins Employed | Reference |
|---|---|---|---|
| 1. | Zn, Cu, Cd, Pb | Chelex-100<br>AG1-X8 | Jeffrey and Uren (1983)<br>Christensen (1989)<br>Sims and Patrick (1978)<br>Camerlynck and Kiekens (1982)<br>Kiekens and Cottenie (1983) |
| 2. | Zn, Cu, Cd, Pb | Ca-saturated resin<br>(Amberlite CG120) | Hodgson *et al.*(1966)<br>Sanders (1983, 1984)<br>Adams and Sanders (1984, 1985) |
| 3. | Zn, Cu, Cd | Amberlite CG120<br>Amberlite CG400 | Bloomfield *et al.*(1976)<br>Bloomfield (1981) |
| 4. | Cd, Pb, Al, Fe | Amberlite IR120<br>Sephadex DEAE A25 | Butterworth and Alloway (1981)<br>Tills and Alloway (1983 a, b, c)<br>Adams and Evans (1989) |
| 5. | Zn, Cu, Cd, Pb | Duolite 225 SRC9 | Tyler *et al.*(1987)<br>Berggren (1989) |
| 6. | Cu | Chelex-100<br>Dowex 50WX4 | Cox *et al.*(1984) |
| 7. | Zn, Cu, Cd | Dowex 50WX4 | Werner (1987)<br>Hodgson *et al.*(1966) |

## 4.2.4. Laboratory Modelling Studies and Heavy Metal Speciation

There have been numerous laboratory studies on the speciation of metals in simplified systems. They range from the exceptionally simple, one metal / one ligand in water (e.g. Turner *et al.*1981), to greater degrees of complexity. Such studies are useful to furthering our knowledge of stability constants, binding sites, competition for the binding site etc., e.g. in the humic and fulvic acids, and how such factors may affect the mobility / adsorptive properties of the metal, e.g. organo-metals, in the soil system (e.g. Elliott and Denneny 1982, Linder and Murray 1987, Stevenson 1976, 1977, Zunino *et al.* 1979). "Complex" laboratory solutions can also be used to assess the experimental determinations and computer predictions of trace metal speciation procedures (McGrath *et al.*1986). The great problem with such controlled studies is that they cannot produce the true complexity that natural waters attain.

Computer models for water speciation began to appear about 20 years ago (Helgeson *et al.* 1969, 1970). Since then, numerous computerised chemical models for natural waters have appeared in the literature - more than 50 according to a review by Nordstrom and Ball (1984). In the early 1980's, some of the most comprehensive and widely applied equilibrium programs were REDEQL2, GEOCHEM and MINEQL (Sposito 1983). REDEQL2 was a predecessor to GEOCHEM, and a program such as GEOCHEM has since evolved into an update program called SOILCHEM. During the 1980's, a program such as GEOCHEM was widely used in trace element chemical speciation (e.g. Behel *et al.*1983, Bingham *et al.*1984, Emmerich *et al.*1982, Mahler *et al.*1980, Mattigod 1981, Mattigod and Page 1983, Mattigod and Sposito 1979, Sposito 1981, 1983, Sposito and Bingham 1981, Sposito *et al.* 1982).

However, two important factors that computer programs do not fully take into account are (Morrison 1987):

(a) The adsorption of metals onto particulates; also interactions at the suspended solid/water interphase.
(b) The presence of organic material - most of which is uncharacterised, especially fulvic acids which form important complexes with heavy metals.

In particular, little is known about the formation constants of complexes involving organic ligands (Evans 1989). Hence, much attention has been

drawn towards metal complexing on humic and fulvic acids (Ewald *et al.*1983, Fitch and Stevenson 1984, Ghosh and Schnitzer 1981, Ryan and Weber 1982a, 1982b, Underdown *et al.*1985) and leaf litter extracts (Blaser and Sposito 1987, Blaser *et al.*1980, Blaser *et al.*1984). Copper is often employed in such studies, especially where spectrofluorometric techniques are used, because of its paramagnetic properties. Information from such studies can help incorporate further data into computer programs such as GEOCHEM (Blaser and Sposito 1987).

As a result of the undoubted drawbacks that analytical and computer speciation studies both face, it seems sensible to combine the two techniques when assessing the forms of metals such as Cd, Cu, Pb and Zn in solution (McGrath *et al.*1986, Mattigod 1981).

In the following sections analytical speciation is considered in Sections 4.4.1-4.4.5, 4.4.9 and computer speciation is considered in Section 4.4.10.

## 4.3. The Solubility of Heavy Metals in the Hallen Wood Soil With Respect to Soil Reaction

### 4.3.1. pH Adjustment of Soil/Peat Sludges

The solubility of heavy metals is mainly influenced by the pH and composition of a soil (Brümmer and Herms 1983). Therefore standard control pH adjustments were made upon three types of sludge:

(a) Hallen Wood soil from 68.5-71cm depth, 0.36% organic matter, 40-50% clay:

(1) Soil: water ratio 1:40.
(2) Soil: water ratio 1:20.

(b) Peat, mainly organic matter, no clay, peat: water ratio 1:40.

Both soil and peat were mixed with oxides of Cd, Cu, Pb and Zn so that they were contaminated with the equivalent of 100 µg/g of metals in the clay and 300 µg/g of the metals in the peat. The metal oxides were first mixed and crushed with a small amount of fine sand so that the eventual mixing within the soil/peat was evenly distributed. A subsample of soil / peat was mixed with deionised water and left to stand and dry out overnight in an oven at 80°C. The sample, once dry, was then crushed and further subsamples were then digested in concentrated nitric acid to be analysed for Cd, Cu, Pb and Zn (Table 4.3.1).

The soil / peat was placed in a 2.5 litre container and was initially mixed with 2 litres deionised water. Calcium hydroxide powder was added to the peat so that the pH might be adjusted to pH8.0. Soil samples pHs naturally settled in a pH8.3-8.6 range. Peat samples were eventually adjusted to pH7.5 (approx). The pHs were taken after allowing the samples to stand overnight.

---

**Table 4.3.1 Analysis of Clay and Peat Samples for Total Cd, Cu, Pb and Zn Content (µg/g dry weight)**

| Metal | Clay | s.d. | Peat | s.d. |
|---|---|---|---|---|
| Cd | 78.8 | 1.84 | 288.3 | 30.67 |
| Cu | 128.1 | 13.32 | 293.3 | 17.94 |
| Pb | 102.8 | 0.76 | 300.0 | 18.03 |
| Zn | 143.0 | 1.54 | 316.7 | 25.17 |

The samples were then mixed by a magnetic stirrer and the pHs measured with a glass electrode. The pHs were mainly adjusted using 1N $HNO_3$, although 1N HCl and 1N $H_2SO_4$ were also used. Each 0.5pH unit decrease was managed over a 1/2 hour period after which aliquots of the suspension were passed through a 0.45μm membrane filter so that three 5ml samples were collected at each 0.5pH interval. These subsequently were diluted in 3ml deionised $H_2O$ and 2ml concentrated $HNO_3$. Samples were then analysed for Cu and Pb mainly by GFAAS, and Cd and Zn by FAAS.

Fig.4.3.1a-d illustrates the effect of pH adjustment on Hallen soil (soil : water ratio 1:40). The pH was adjusted with three different acids (1N $HNO_3$, HCl, $H_2SO_4$). The main features of note are:

(a) All four metals increased in solubility with decreasing pH, the relationship being of a curvilinear nature.
(b) Zn and Cd rapidly increased in solubility in a linear fashion at pHs below pH5.5, whereas Cu and Pb had very low solubility at pH5.0 and above.
(c) Zn and Cd were far more soluble than Cu and Pb at low pH, and Zn and Cd only entered the same range of solubility that Pb and Cu covered at >pH6.0

The distinct "bend" in the regression curves indicates rapidly increasing metal solubility below a particular pH (Tyler *et al.*1987). Any variations in the curvilinear nature of the Pb/Cu curves could have been due to the low concentration ranges that they have been plotted over, although the effect of Lewis base ligands might have played a part in complexing or precipitating the metals e.g. the lower solubility of Pb in the sulphate system might be the result of lead sulphate precipitation.

Fig.4.3.2a-b demonstrates the effect of changing pH on mineral soil (MS) and organic matter (OM) systems. In this instance the soil: water ratio was 1:20 and the peat: water ratio was 1:40. Despite the different metal and constituent loadings in both systems (also with respect to Fig.4.3.1a-d) the curvilinear relationship was still maintained. Furthermore, Zn and Cd were still more soluble than Pb and Cu at the lower pH range - at pH5.5 Zn and Cd concentrations attained the range of Pb and Cu concentrations at pH3.0. Considering that the peat system had a greater quantity of metals (15,000μg of each metal) and only one half the weight of adsorbing substrate (50g of peat) in comparison to the clay system (10,000μg of each metal; 100g of clay) it might be supposed that more metal should have been detected in solution within the

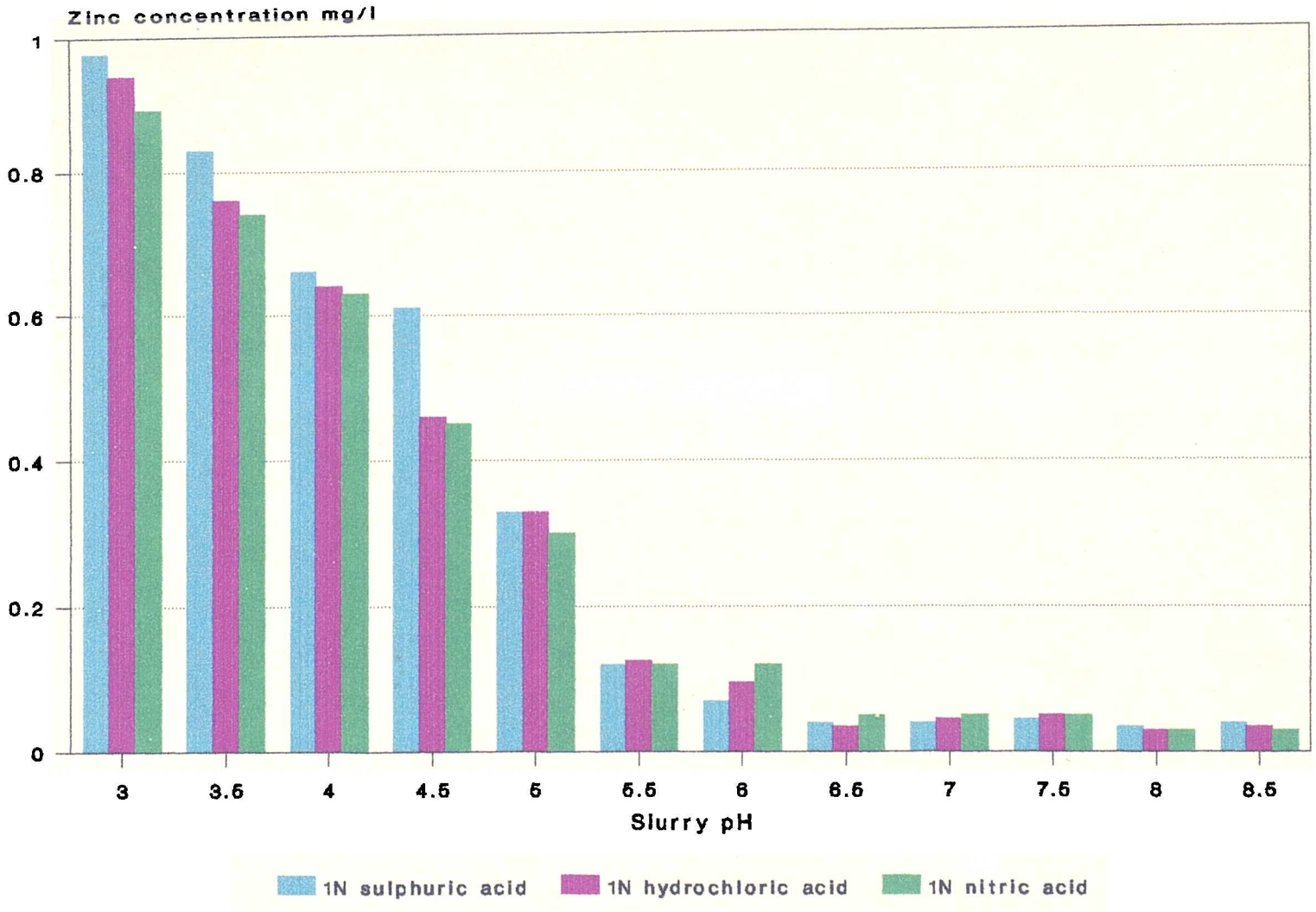


**Fig.4.3.1a Zinc Solution Concentration with change of Slurry pH; pH altered by using three different acid treatments.**

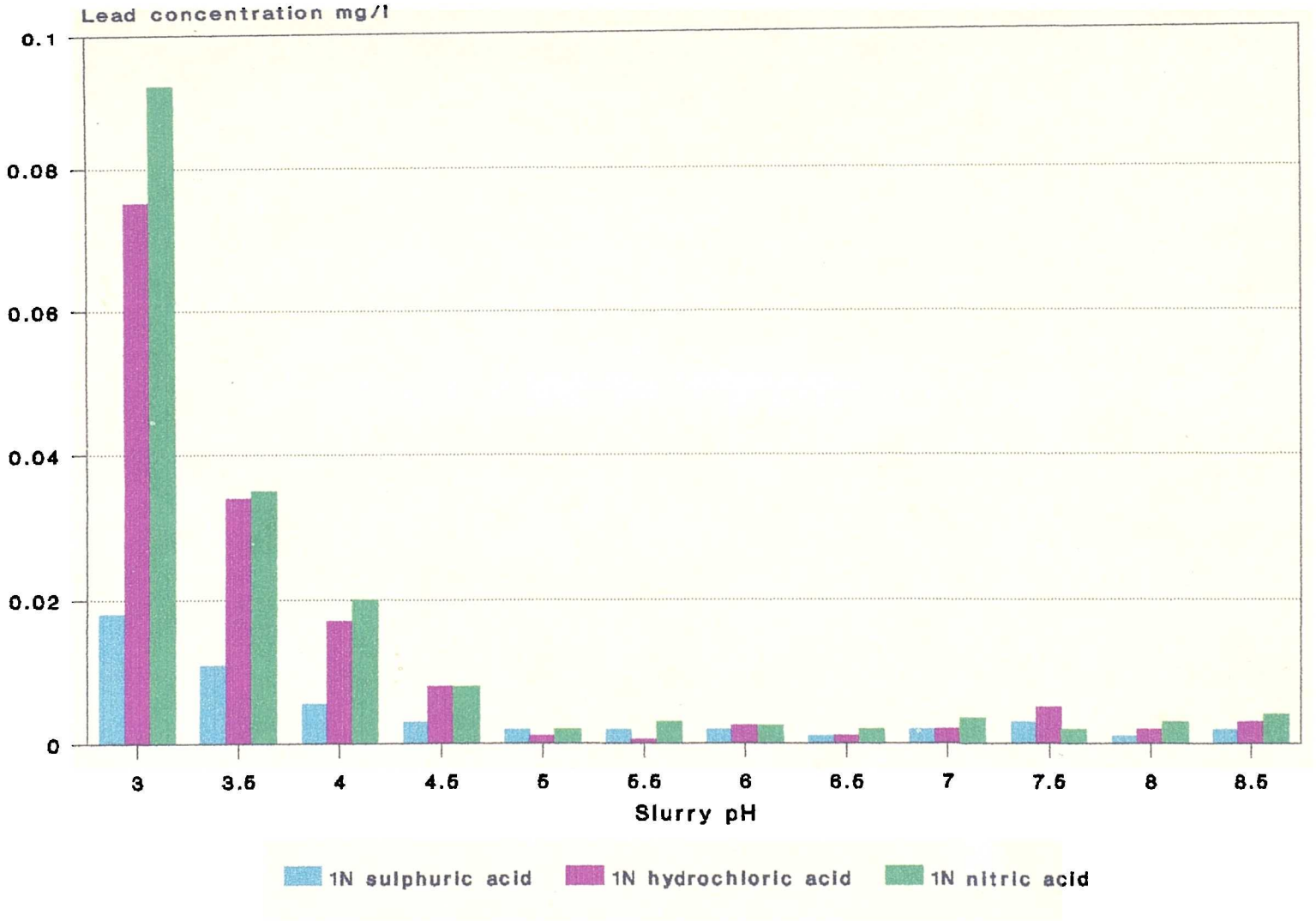


**Fig.4.3.1b Lead Solution Concentration with change of Slurry pH; pH altered by using three different acid treatments.**

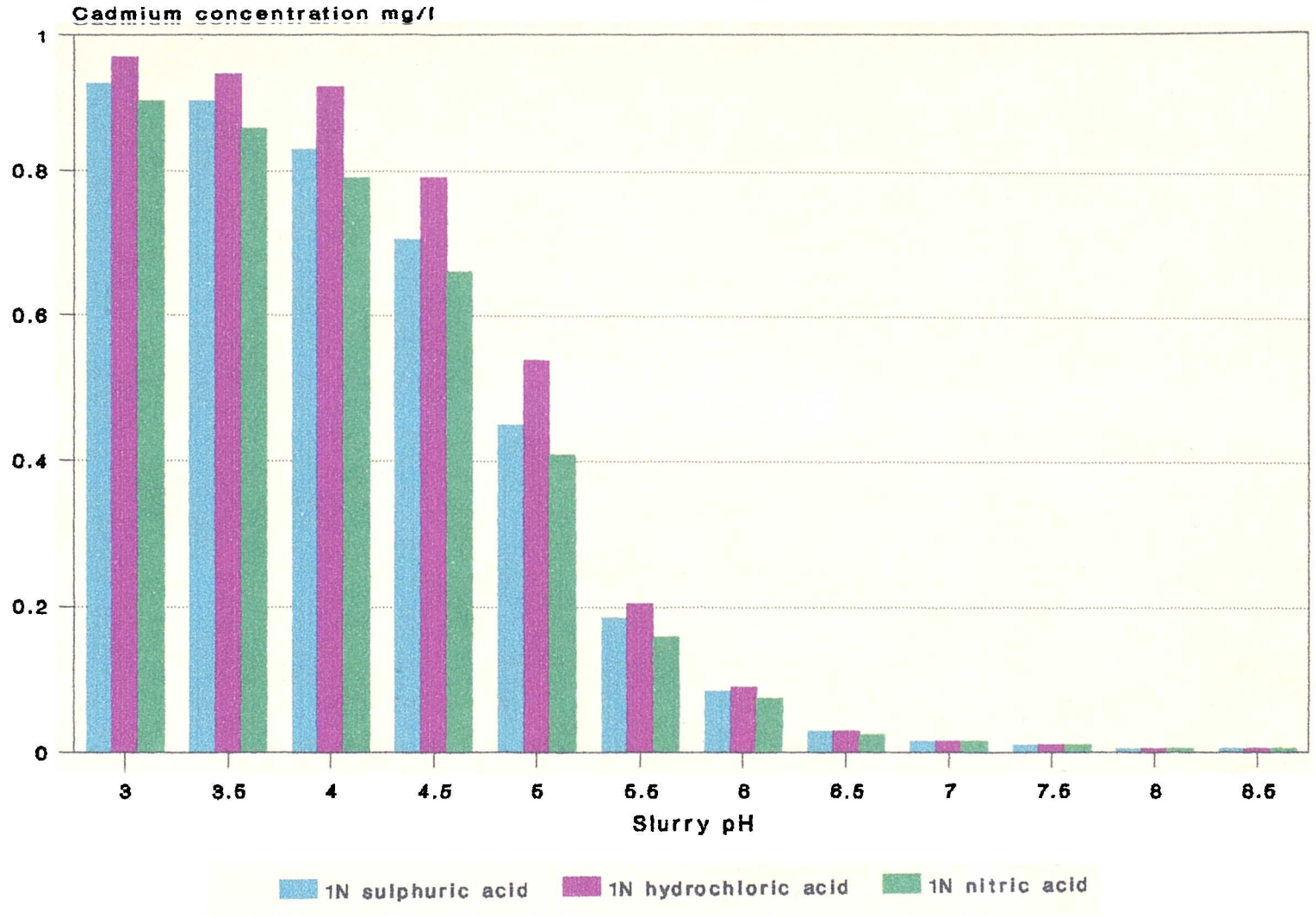


Fig.4.3.1c Cadmium Solution Conc.(mg/l) with change of Slurry pH; pH altered by using three different acid treatments.

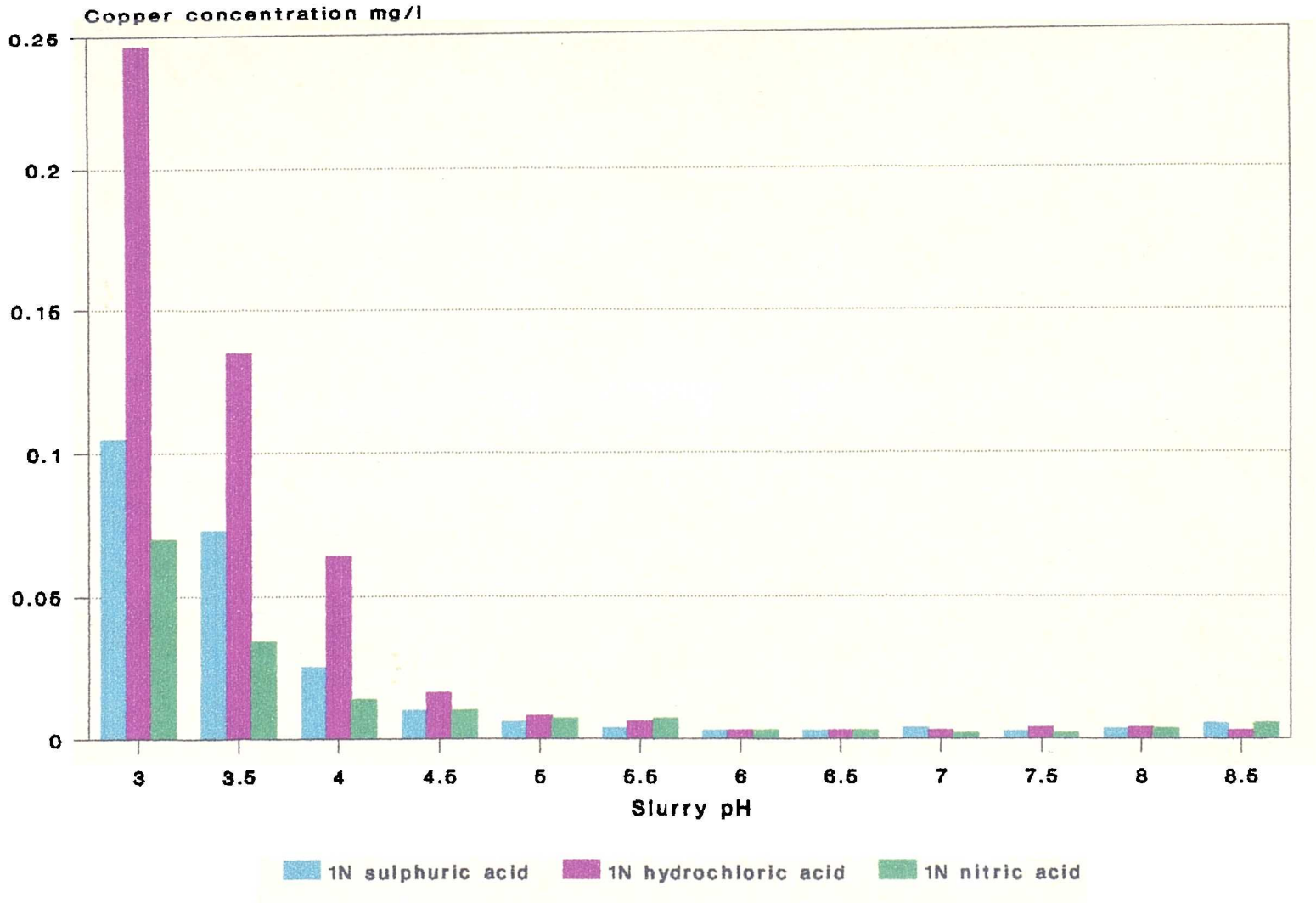


**Fig.4.3.1d Copper Solution Concentration with change of Slurry pH; pH altered by using three different acid treatments.**

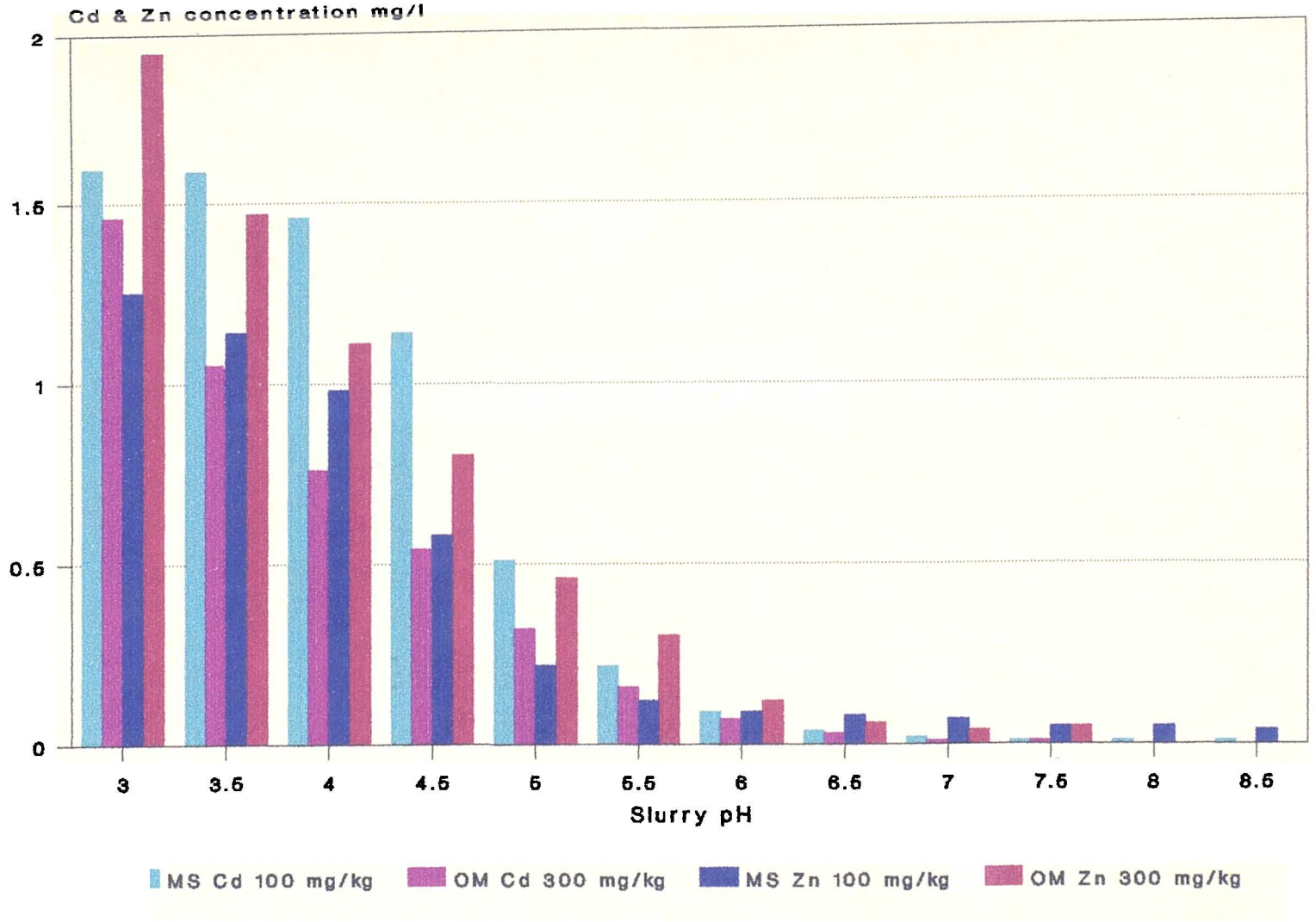


**Fig.4.3.2a Cd & Zn Solution Conc.(mg/l) with change of pH upon mineral soil (MS) & organic matter (OM) Slurries.**

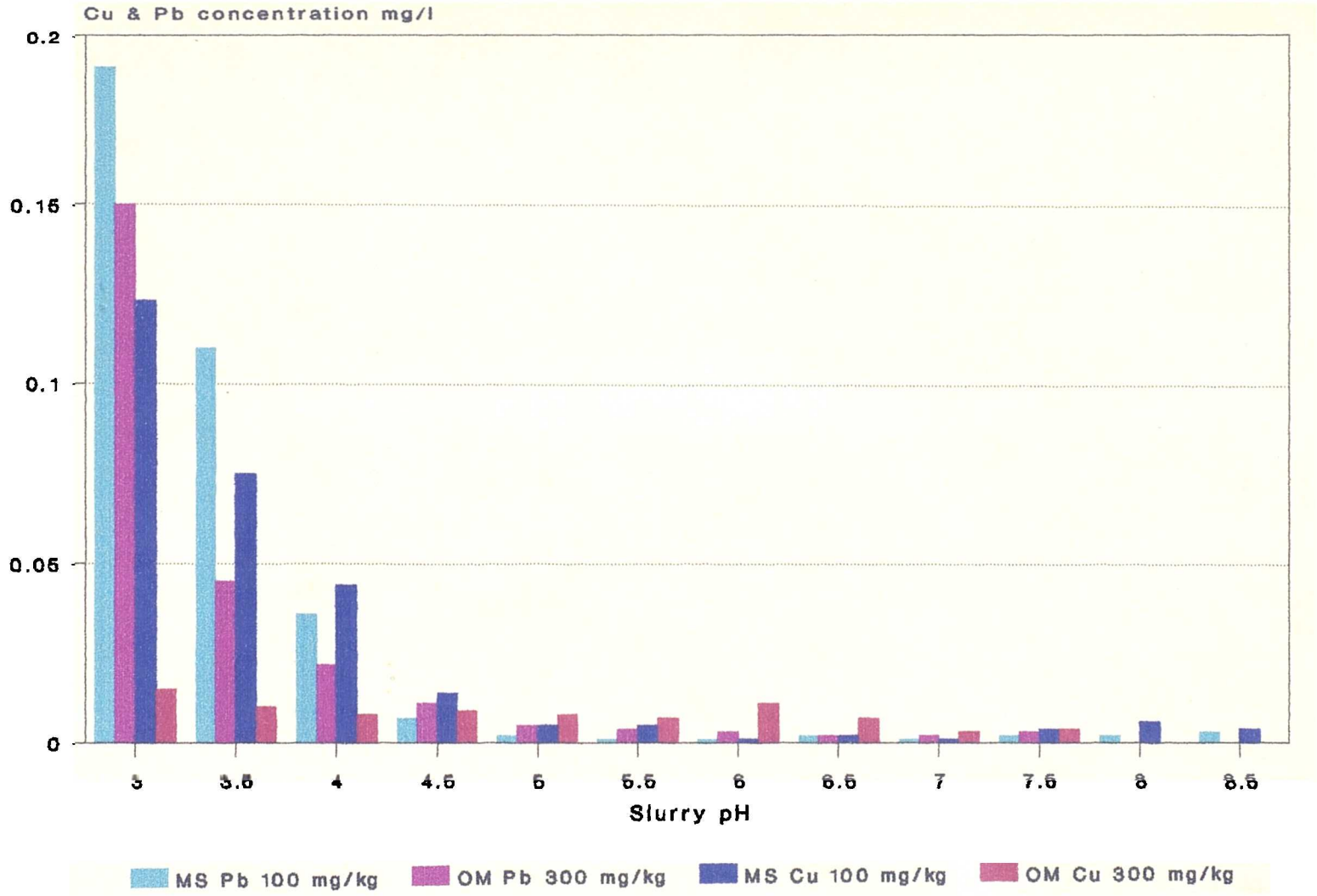


Fig.4.3.2b Cu & Pb Solution Conc.(mg/l) with change of pH upon mineral soil (MS) & organic matter (OM) Slurries.

former system. The fact that this was not so probably indicates the high affinity that heavy metals have for organic matter. This is more clearly featured in Fig.4.3.3a-b. These figures illustrate four important things:

(a) The proportion of metals in solution was less in the peat system than for the clay system despite the fact that there was three times the metal concentration in the peat system.

(b) The metals that were least affected by the peat system (in relation to the clay system) were Pb and Zn. Cu and Cd were more noticeably influenced in their solubility in the peat system.

(c) An idea of the potential mobilities of the metals within the systems was gained. The mobilisation effect of pH followed the order:

$$Cd > Zn \gg Pb = Cu \quad \text{in the Hallen clay system}$$
$$Zn \geq Cd \gg Pb \geq Cu \quad \text{in the peat system}$$

(d) In proportional terms, the important pH range for Cd and Zn solubility would appear to be in the pH5.5-6.0 region. As for Pb and Cu, the pH4.0-4.5 region would seem more important in controlling their solubility, although both these metals were clearly more insoluble (with respect to Cd and Zn) over the entire pH range covered.

The main drawback of the results in Figs.4.3.1-4.3.3 is that the systems used are grossly dilute and "unreal" in terms of a "true" soil system. The major advantage of a dilute system is that pH adjustments can be more effectively made on the system as soil constituents have a large buffering capacity - i.e. the more dilute the system the easier it is to control the stability of the solution pH for a more prolonged period of time. The other advantage of a dilute system is that if a volume of acid (or alkali) is being added to it over a range of pH then the volume added has a minimal dilution effect on the system. In conjunction with the sample solution required for analysis, the overall displacement or addition to the bulk volume was $\leq \pm 3\%$.

Similar experiments have used equilibration times of 30 minutes or longer (Adams and Sanders 1984, Brümmer and Herms 1983). Adams and Sanders (1984) used $HNO_3$ and KOH to adjust system pHs, and used a dry solid to water ratio of 8 grams to 400mls i.e. 1:50. Brümmer and Herms (1983) found that in soils the solubility of Cu and Pb increased as the pH dropped lower than pH5 and 4 respectively, whereas Cd and Zn strongly increased in solubility as pH dropped below pH6. Also, Adams and Sanders (1984) suggested that

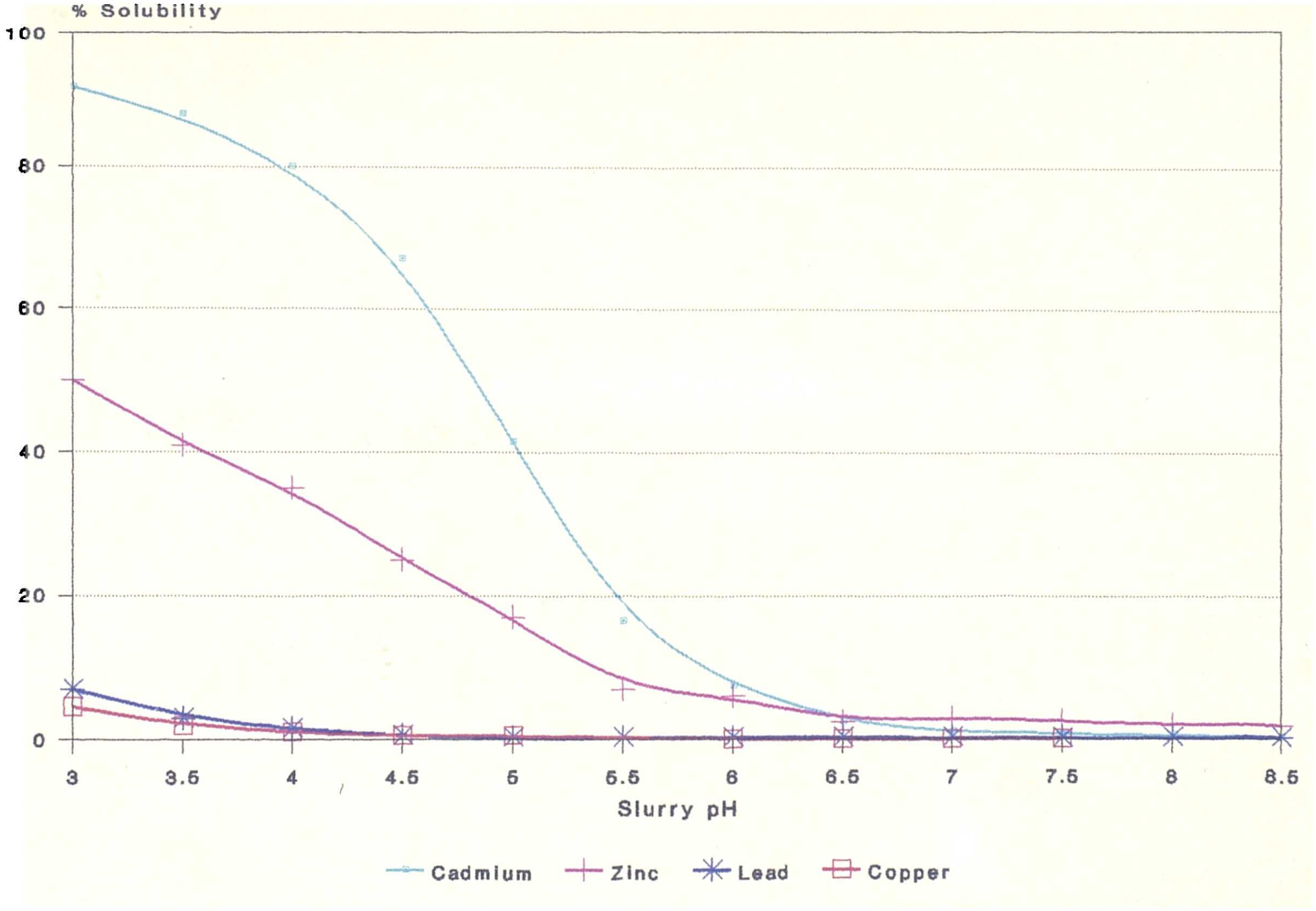


**Fig.4.3.3a % Solubility of Heavy Metals with change of pH upon mineral soil (MS) slurry.**

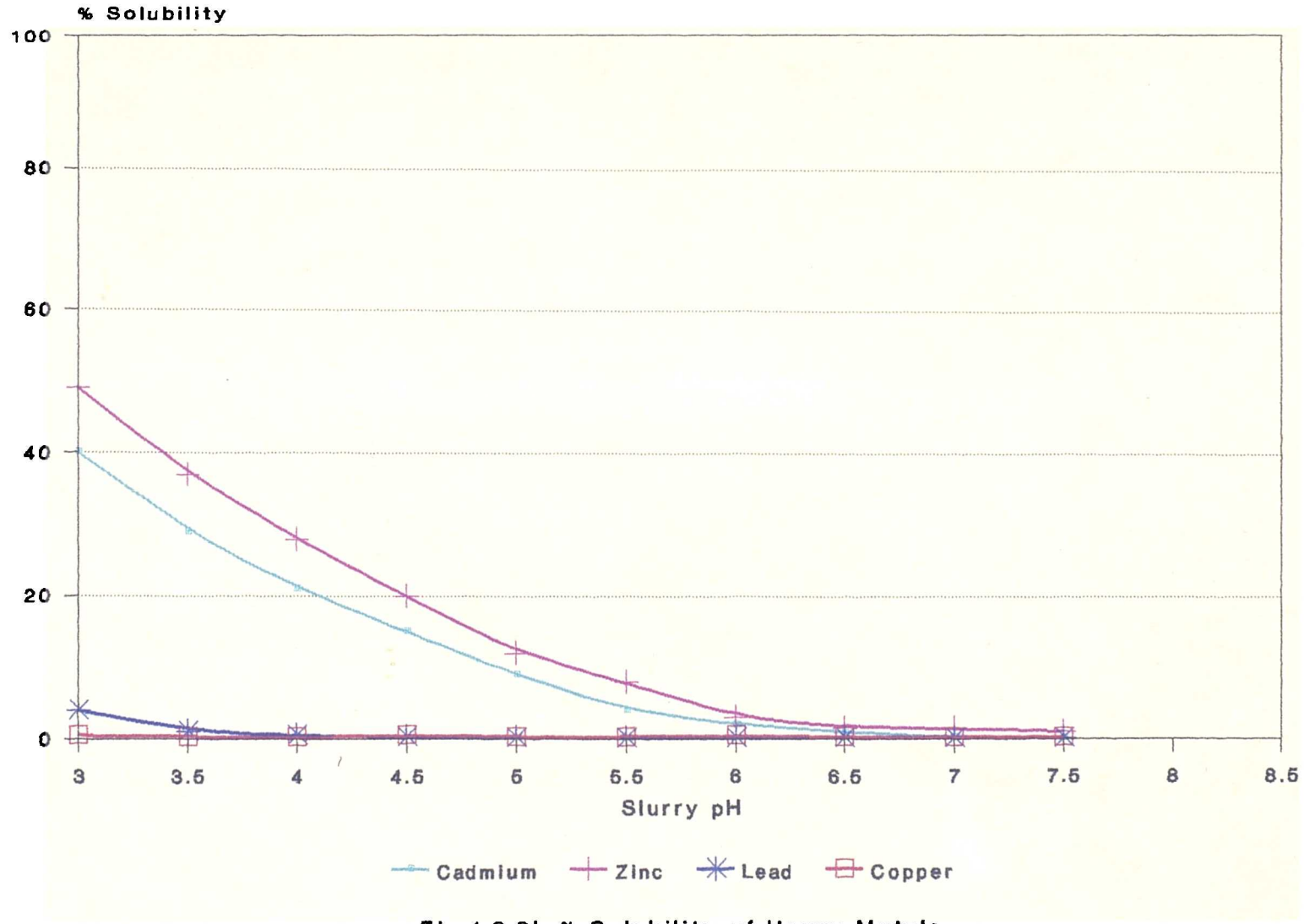


**Fig.4.3.3b % Solubility of Heavy Metals with change of pH upon organic matter (OM) slurry.**

pH4.5 and pH5.8 were important threshold values for Cu and Zn, respectively, in metal-loaded sewage sludge. Such results tend to ratify with those results shown in Figs.4.3.1-4.3.3. Brümmer and Herms (1983) also proposed that peat immobilised heavy metals in the order Cu > Cd > Zn > Pb. Although this order does not hold true for metals in Figs.4.3.2-4.3.3, there is, nevertheless, the suggestion that the peat affected the solubility of the metals in relation to the clay soil in the order Cu, Cd > Zn, Pb. However, Brümmer and Herms (1983) also demonstrated that fresh organic matter (hay) mobilised heavy metals in the order Cu > Cd > Zn > Pb. Therefore, there is an indication that different forms of organic matter will affect the solubility of heavy metals in different ways.

## 4.3.2. Hallen Wood Heavy Metal Solubility

See Section 4.4.1 for methodology. In Figs.4.3.4a-d for Hallen Wood, the relationship between soluble metals and pH is not quite as clear cut as previous Figures in Section 4.3.1. have demonstrated. It would appear that all four metals decrease in solubility with increasing pH; however, other factors such as soil depth should also be seen as probably being influential upon the distribution of soluble heavy metals within the Hallen profile (c.f. Chapter 3, Section 6).

Fig.4.3.5a highlights the fact that in Hallen Wood the order of metal mobility in the solution phase was:

$$Cd > Zn \geq Cu > Pb$$

Perhaps what is most striking about the Hallen Wood metal distributions was the very low solubility of Pb and the reasonably high solubility of Cu (in relation to Cd and Zn). This latter feature is somewhat intriguing, but could help to explain how Cu manages to be relatively plant available in relation to Zn (see Chapter 5, Section 3). The low % solubility values for the four metals at pH4.0 - pH4.35 were associated with the high organic matter contents within the L, F, H and 0-1cm layers. In Haw Wood (Fig.4.3.5b) in the top 11cm of soil, the % solubilities of metals were very low (in comparison to Hallen topsoil) despite the very high metal concentrations in the Haw topsoil. At pH5.0 in the litter (L, F, H), the solubilities are low for all four metals. Once within the mineral soil (between pH5.20 and pH5.65 [0-6cm depth]) the solubilities of Zn and Cu were enhanced to that of Cd. Zn appeared to be more

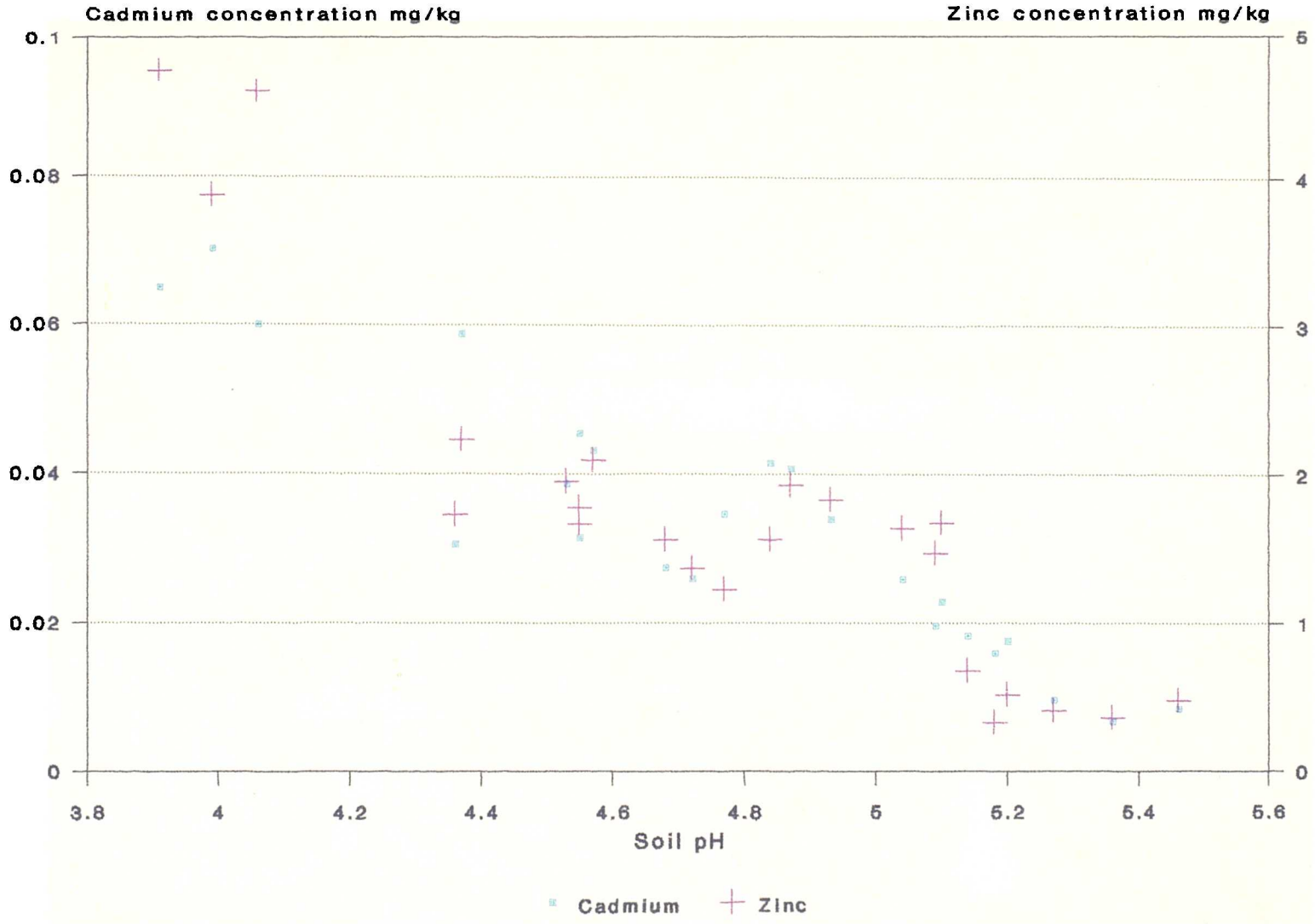


**Fig.4.3.4a Soil solution concentrations of Cd and Zn in Hallen Wood.**

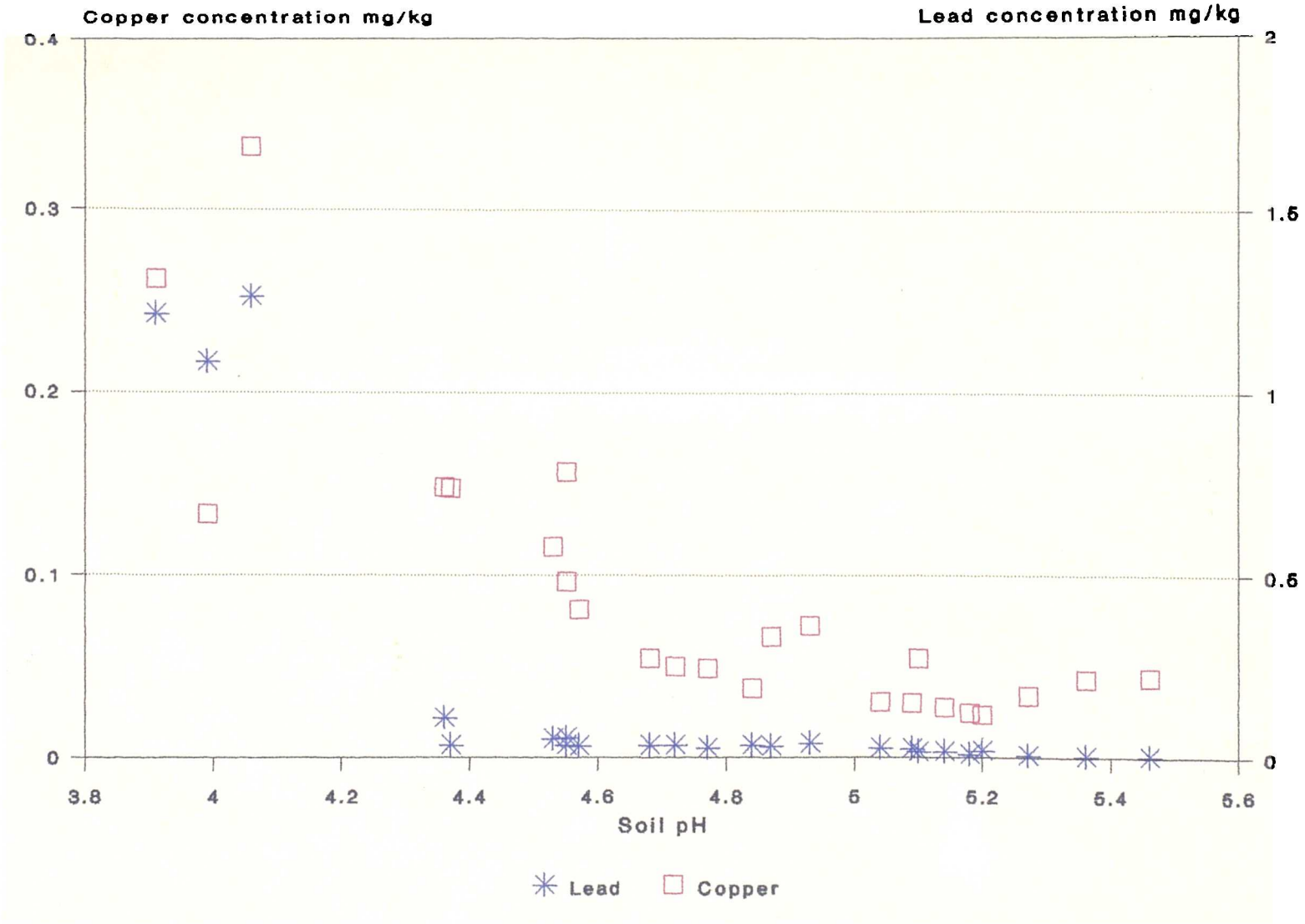


**Fig.4.3.4b Soil solution concentrations of Cu and Pb in Hallen Wood.**

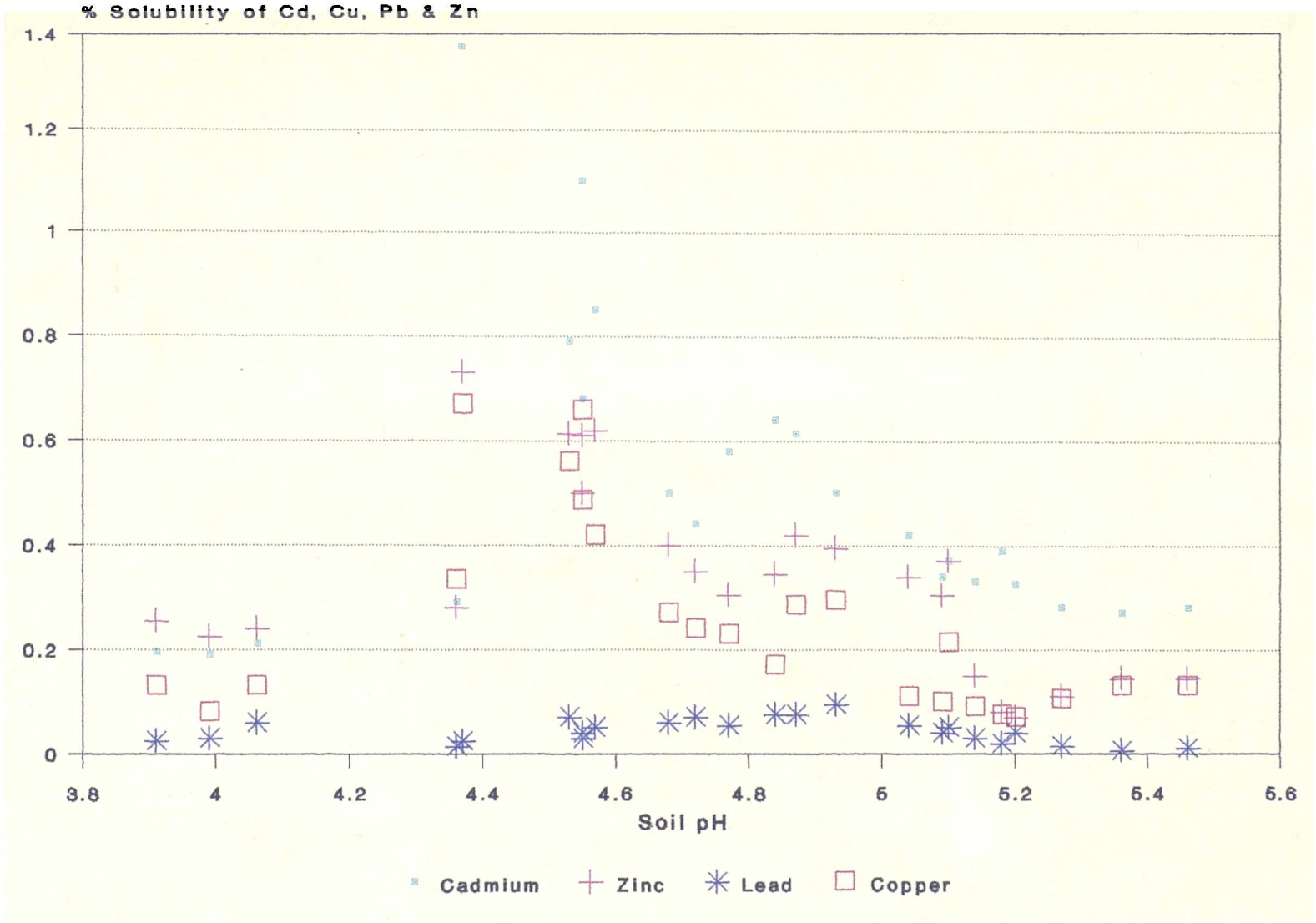


**Fig.4.3.5a % Solubility of Cd, Cu, Pb & Zn in Hallen Wood Soil.**

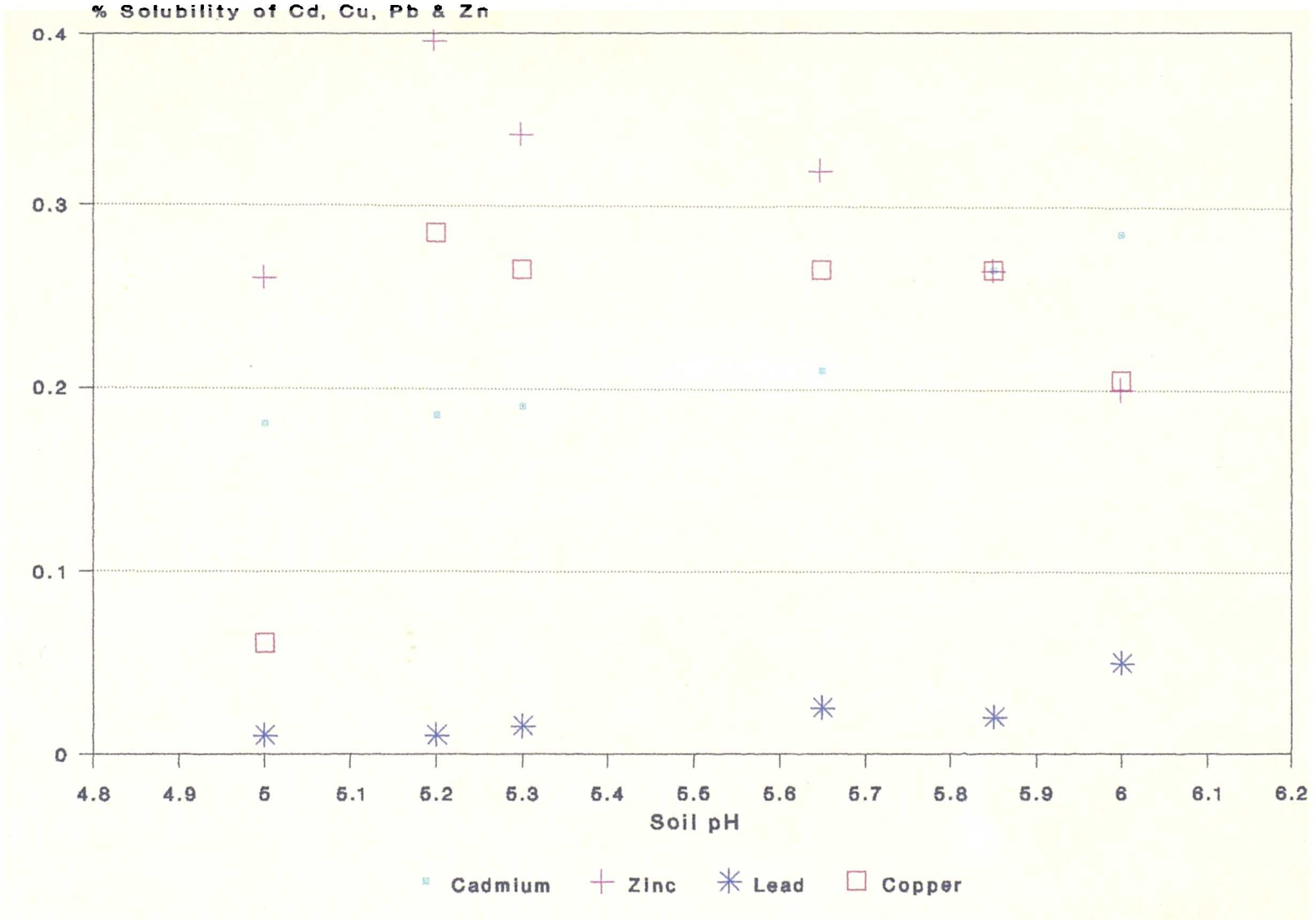


**Fig.4.3.5b % Solubility of Cd, Cu, Pb & Zn in Haw Wood Soil.**

soluble or as soluble as Cd within the litter layers and the mineral soil which contained higher organic matter contents in both of the woodlands (in soil with >3.5% carbon). This corroborates with the findings in Fig.4.3.3b in peat.

## 4.4. The Speciation of Cd, Cu, Pb and Zn in Hallen Wood and Haw Wood Soils

### 4.4.1. Water Soluble Cations and Anions

These were extracted from the soil be shaking 20g of soil in 50ml deionised water in polyethylene bottle for one hour. The suspensions were then filtered through a Whatman No.50 filter paper. Cations were then measured by AAS (see Appendix A) and the inorganic anions were measured by ion-exchange chromatography by HPLC (see Appendix B).

### 4.4.2. Water Soluble Heavy Metals for Determination of Speciation

The main problem encountered was to obtain enough solution to be used for the speciation procedure without drastically increasing the soil: solution ratio used in Section 4.4.1. A ratio of 1:4 was used instead of 1:2.5 so that 80ml of solution was available for the speciation procedure: 50ml for the purpose of ion-exchange and 30ml for recording of the solution pH. 30g of soil were shaken for 1 hour in 125ml of deionised water. The resulting suspension was then filtered through a Whatman No.50 filter paper. The filtered solution was then filtered again through a 0.45μm Millipore membrane filter.

A procedure similar to that described by Tills and Alloway (1983a, 1983b, 1983c) was used to analytically determine heavy metal species in the soil solution as cationic, anionic, neutral and low polar organic forms. The general outline of the procedure is illustrated in Fig.4.4.1. The cation resin, Amberlite IR120, and the anion resin, DEAE A25 Sephadex, were used to separate metals into cationic, anionic and neutral forms. Resins were soaked for 24 hours in deionised water to allow for full resin swelling. The Amberlite resin was then soaked in 0.5M HCl overnight, followed by 0.5M NaOH overnight, and finally soaked and washed in deionised water. A similar procedure was used for the Sephadex resin, but this time the resin was primarily soaked in 0.5M NaOH, then 0.5M HCl, followed by 1M $CH_3COOH$ and finally soaked and washed in deionised water. Such procedures enable the resins to be cleaned of any trace metal impurities.

Acid washed plastic syringes and glass wool were used to pack the resins creating simple ion-exchange columns. Resin slurry (in deionised water) was added to the columns to fill the syringes to a volume of 3ml (≡ 0.5g dry weight Sephadex beads ≡ 1.5g dry weight Amberlite beads). As the bead diameters

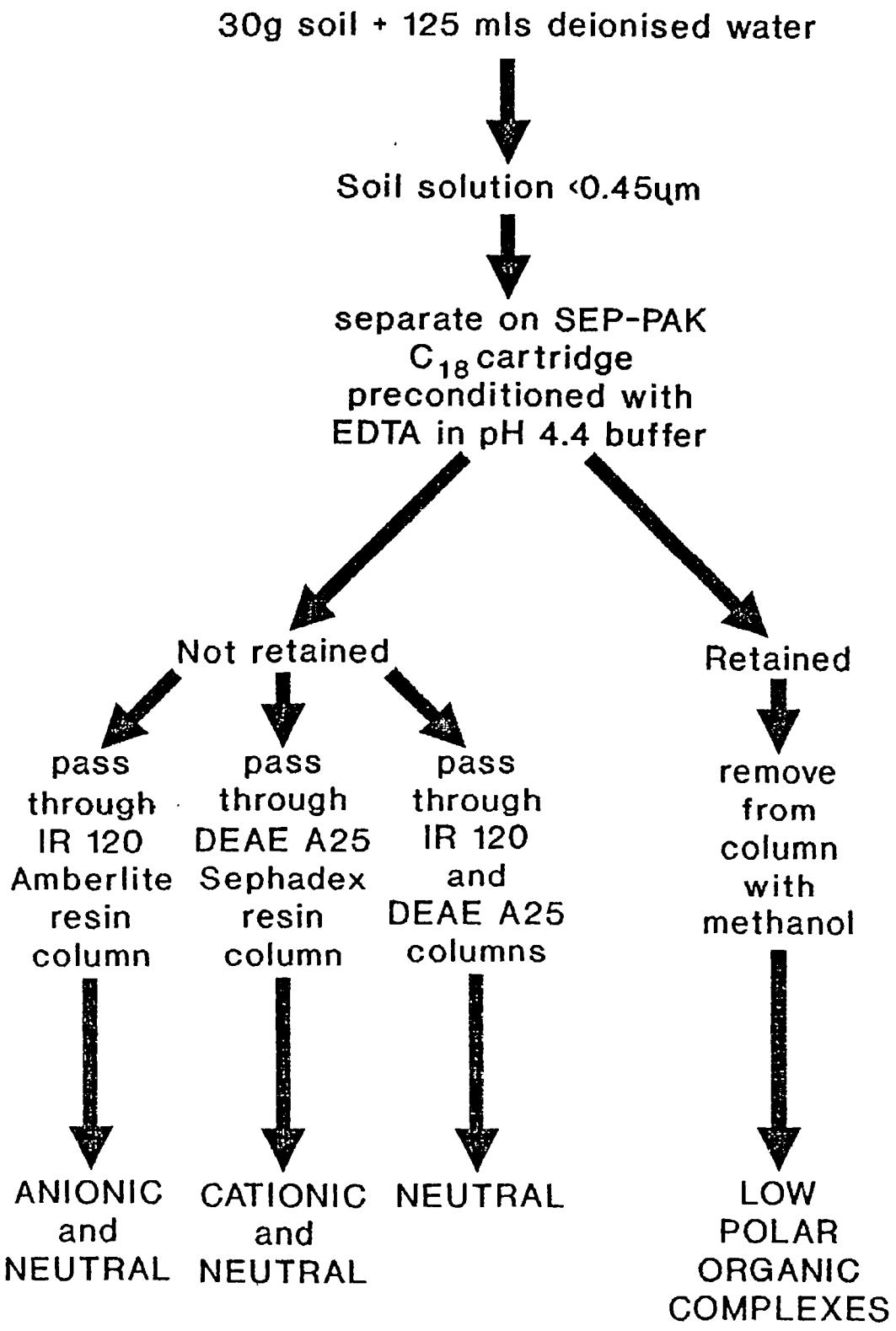


Fig.4.4.1 Speciation procedure adapted from Tills and Alloway (1983)

for the two resins were different, flow rates were normalised by putting the larger diameter Amberlite beads into narrower 5ml plastic syringes, and the smaller diameter Sephadex beads into wider 10ml plastic syringes. Flow rates were then standardised to 2ml / min by using syringe needles of the right aperture. Before passing a sample through the ion-exchange systems a small subsample aliquot was passed through the resin system to take into account adsorption effects (e.g. on the wall of the syringe) and the displacement of deionised water from the void volume of the system.

The SEP-PAK $C_{18}$ cartridge is a compact reverse phase chromatographic column. The hydrophobic resin contains organic groups chemically bonded to porous silica. They have been used with some success by Florence (1982), Mills *et al.*(1982) and Donat *et al.*(1986). SEP-PAK $C_{18}$ cartridges have the added advantage over polystyrene resins that irreversible adsorption via charge transfer interactions cannot occur (Mackey 1984). However, the SEP-PAK $C_{18}$ does not remove all the organo-metallic species (Mills and Quin 1981) as very polar compounds are only partially removed from waters (Mackey 1984). The SEP-PAK $C_{18}$ cartridges are normally conditioned with a preliminary 10ml of deionised water, followed by 2ml of methanol and finally a further 10ml of deionised water. Further conditioning was required, however, in order to remove zinc contaminants from the cartridge (Fig.4.4.2). Steps 1-4 were separate 10ml treatments of the cartridge with 0.05g Na-EDTA in 250ml acetic acid/sodium acetate buffer at pH4.4. Chelating agents such as EDTA are recommended for desorbing metals from internal surfaces (Lydersen *et al.* 1987). This served to remove most of the available zinc. Steps 5-10 of water washings helped remove any remaining zinc. Between steps 3 and 4 the cartridge was conditioned with methanol.

In order to ensure that the zinc contamination had been sufficiently dealt with, some preliminary samples were used with cartridges prepared in the above method. Two samples were prepared - one from the fermentation layer and one from the 0-1cm layer of the Hallen Wood soil. 10ml of a sample was passed through a conditioned SEP-PAK cartridge. The solution that passed through was retained for analysis. The SEP-PAK cartridge was then washed with 10ml of deionised water - this was discarded. Then 2ml of methanol followed by 8ml of deionised water were passed through the cartridge - this was collected for analysis (low polar organic complexes). The original solution was also retained for analysis. All analyses were carried out on the FAAS (see Table 4.4.1). A further test was carried out on the Hallen fermentation layer where two replicates were taken. The two replicates were themselves replicated

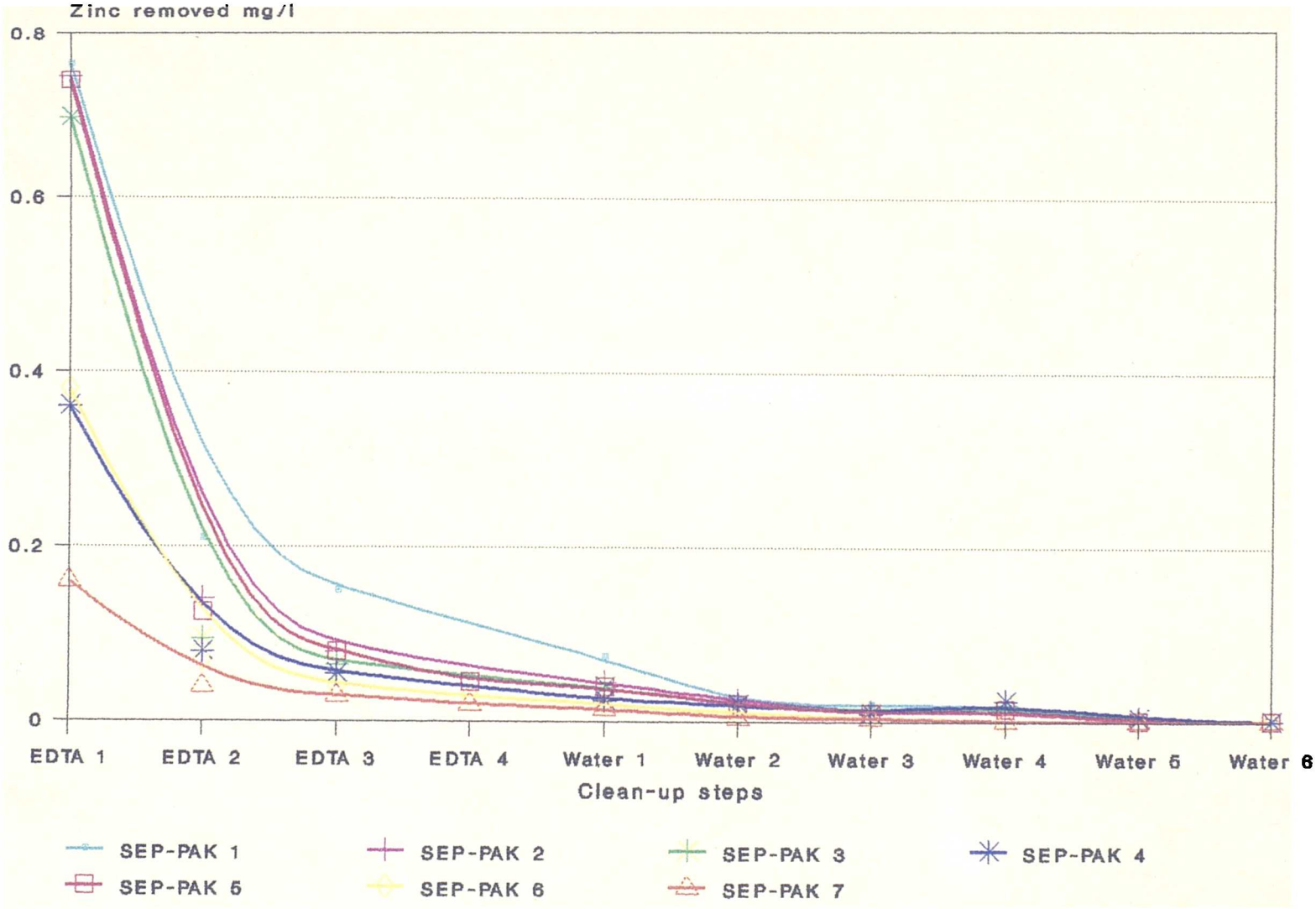


**Fig.4.4.2 Steps taken to remove SEP-PAK C18 cartridges of Zinc contaminants.**

**Table 4.4.1 Total Zinc in Solutions and the Proportion of Zinc Retained and Not Retained by the SEP-PAK $C_{18}$ Cartridge (μg/ml)**

| | | Fermentation | % Recovered | 0-1cm | % Recovered |
|---|---|---|---|---|---|
| (a) | Total Solution Zn | 1.812 | | 0.764 | |
| (b) | Zn Not Retained | 1.656 | 91.4 | 0.690 | 90.3 |
| (c) | Zn Retained | 0.156 | 8.6 | 0.062 | 8.1 |
| | (b) + (c) | 1.812 | 100 | 0.752 | 98.4 |

**Table 4.4.2 Total Zinc in Solutions and the Proportion of Zinc Retained and Not Retained by the SEP-PAK $C_{18}$ Cartridge (μg/ml)**

| | | Sample A | | | | Sample B | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Sub Sample 1 | % Rec | Sub Sample 2 | % Rec | Sub Sample 1 | % Rec | Sub Sample 2 | % Rec |
| (a) | Total Soln Zn | 1.879 | | 1.879 | | 1.639 | | 1.697 | |
| (b) | Zn not retained | 1.616 | 86.0 | 1.635 | 87.0 | 1.493 | 91.1 | 1.500 | 88.4 |
| (c) | Zn retained | 0.143 | 7.6 | 0.097 | 5.2 | 0.126 | 7.7 | 0.187 | 11.0 |
| | (b) + (c) | 1.759 | 93.6 | 1.732 | 92.2 | 1.619 | 98.8 | 1.687 | 99.4 |

---

twice. The results from this study are shown in Table 4.4.2. In general the % recovery was fairly good with the % recovery in Fermentation 1 being slightly suppressed (Table 4.4.2). What is important is that any Zn contamination within the SEP-PAK appeared to have been dealt with. If excess Zn was still available in the cartridge, then a % recovery well in excess of 100% might have been expected.

Once a sample had been processed by the SEP-PAK procedure, the solution containing the non-retained species was processed further by using resin

columns as illustrated in Fig.4.4.1. After a preliminary 3ml aliquot of sample had passed through the column, a further 8ml of sample were then passed through and collected to be stored in 2ml concentrated $HNO_3$ (sample in 20% $HNO_3$). In the case of neutral metal species, after the 3ml aliquot had passed through the first resin column, a further 11ml were collected. The second column was then conditioned with 3ml of the previous 11ml collected. The final 8ml were then collected and stored in 2ml concentrated $HNO_3$. Blank samples were carried out in exactly the same way. All sampling of soil layers and blanks were carried out in triplicate. With hindsight, as the solution concentrations were low, it might have been better to carry out the sampling in quintuplicate so that the standard error of some layers would have been improved. However, the technique used was found to be much more time-consuming than had been initially envisaged, in order to ensure that contamination was minimal and the clean-up of the exchange / chromatograph systems was thorough. Zn concentrations were measured by FAAS, whereas Cd, Cu and Pb were measured by GFAAS (See Appendix A).

### 4.4.3. Heavy Metal Speciation Analytical Results for Hallen Wood Soils

The results for heavy metal concentrations in the soil solution were of a similar range of magnitude whether collected by the method described in Section 4.4.1 and measured by FAAS, or collected by the method described in Section 4.4.2 and measured by FAAS in the case of Zn or GFAAS in the case of Cd, Cu and Pb (c.f. results of water soluble metals in the appendices). If anything, the results from the method in Section 4.4.2 were marginally higher. The fact that the soil pH (1:2.5 soil: water ratio) and soil solution pH (1:4 soil: water ratio) were not markedly different probably helps to explain this (see Fig.4.4.3) and suggests that the water chemistry in the 1:4 mix was not very much different from the 1:2.5 mix; the same can also be said for Haw Wood.

Fig.4.4.4 illustrates the concentration of metals found as cationic, anionic, neutral or low polar organic forms. The most striking feature of Fig.4.4.4 is the overwhelming abundance of Cd and Zn cationic forms throughout the Hallen profile. Cationic forms were also important for Pb, but not to the same degree as for Cd and Zn. However, Cu was totally different and low polar organics and anionic forms clearly dominated. In Fig.4.4.5 a clearer understanding of the proportional distribution of metal species down the Hallen profile can be gained. Cd and Zn have generally > 70% of their metal forms in

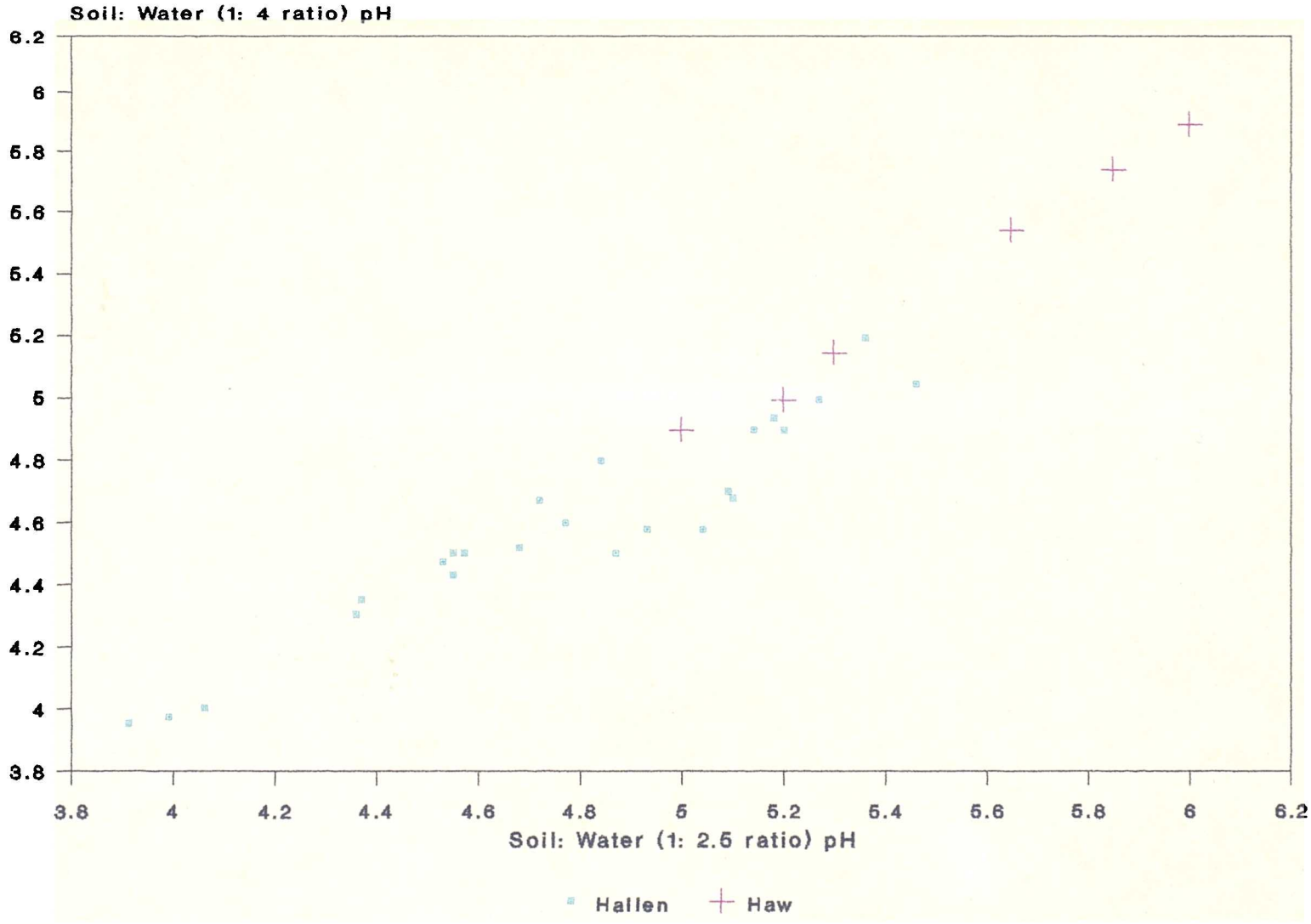


**Fig.4.4.3 Relationship between Soil pH and Soil Solution pH in Haw/Hallen Wood.**

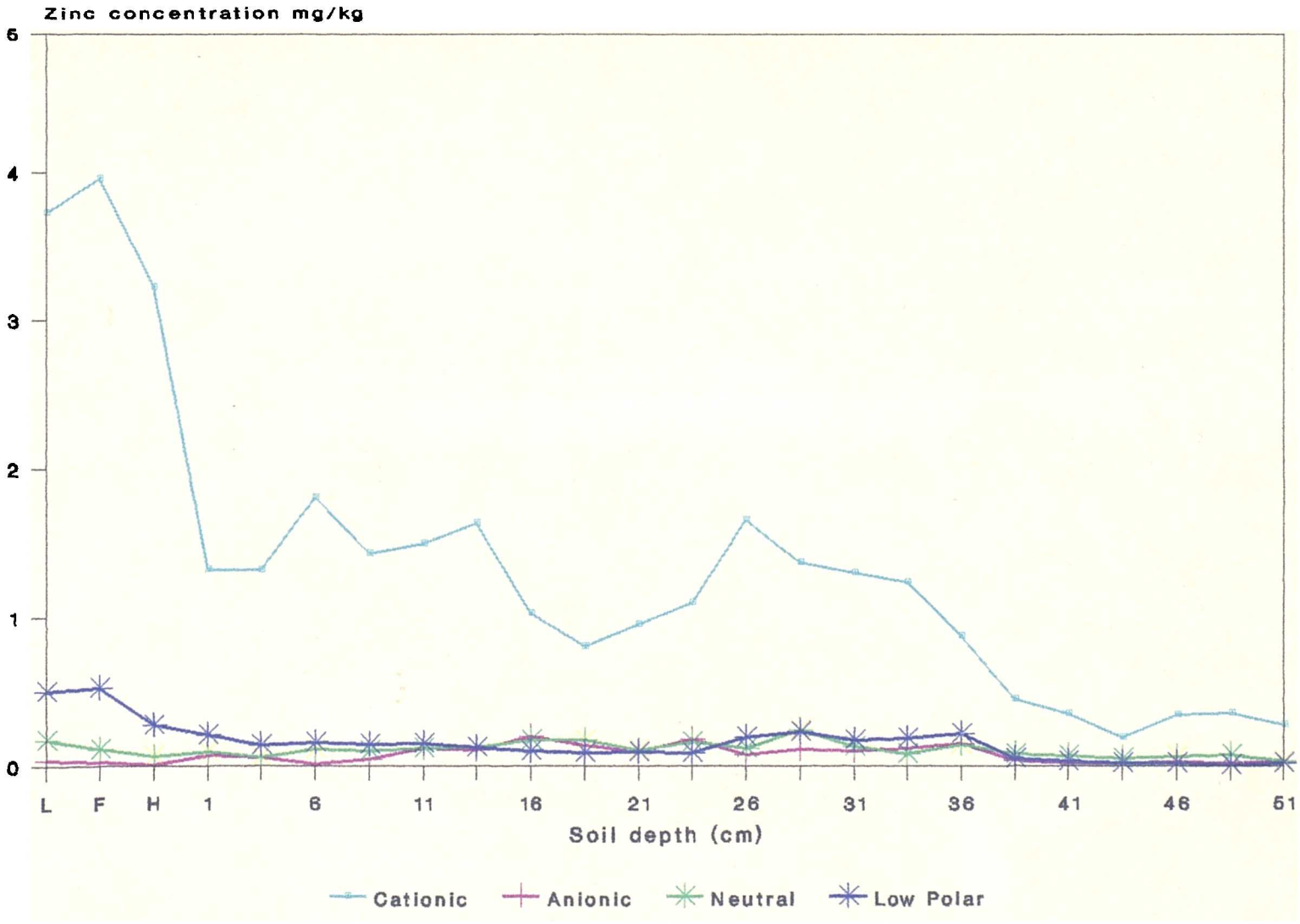


**Fig.4.4.4a Zinc speciation of water extracts of Hallen Wood (1987) soil.**

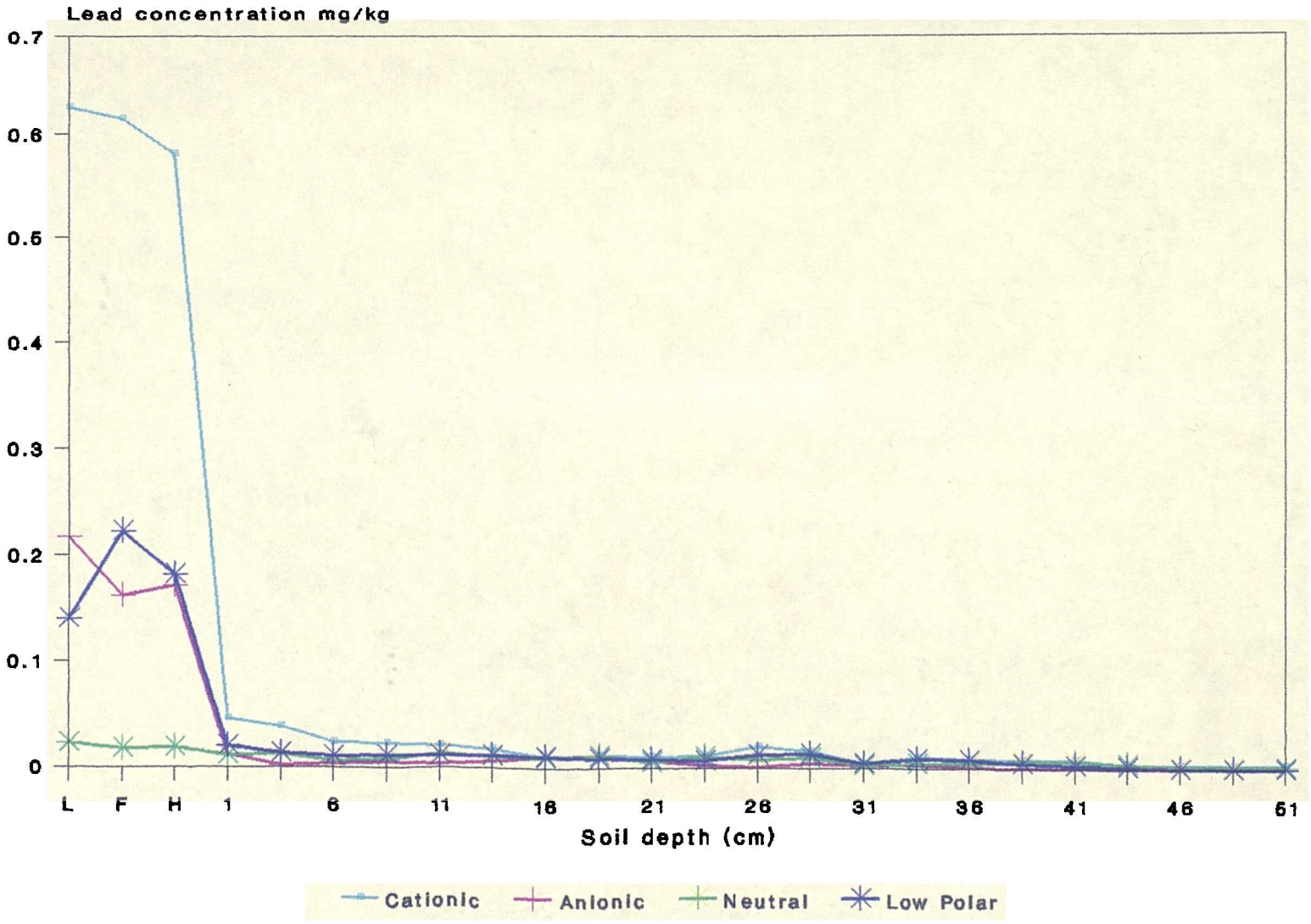


Fig.4.4.4b Lead speciation of water extracts of Hallen Wood (1987) soil.

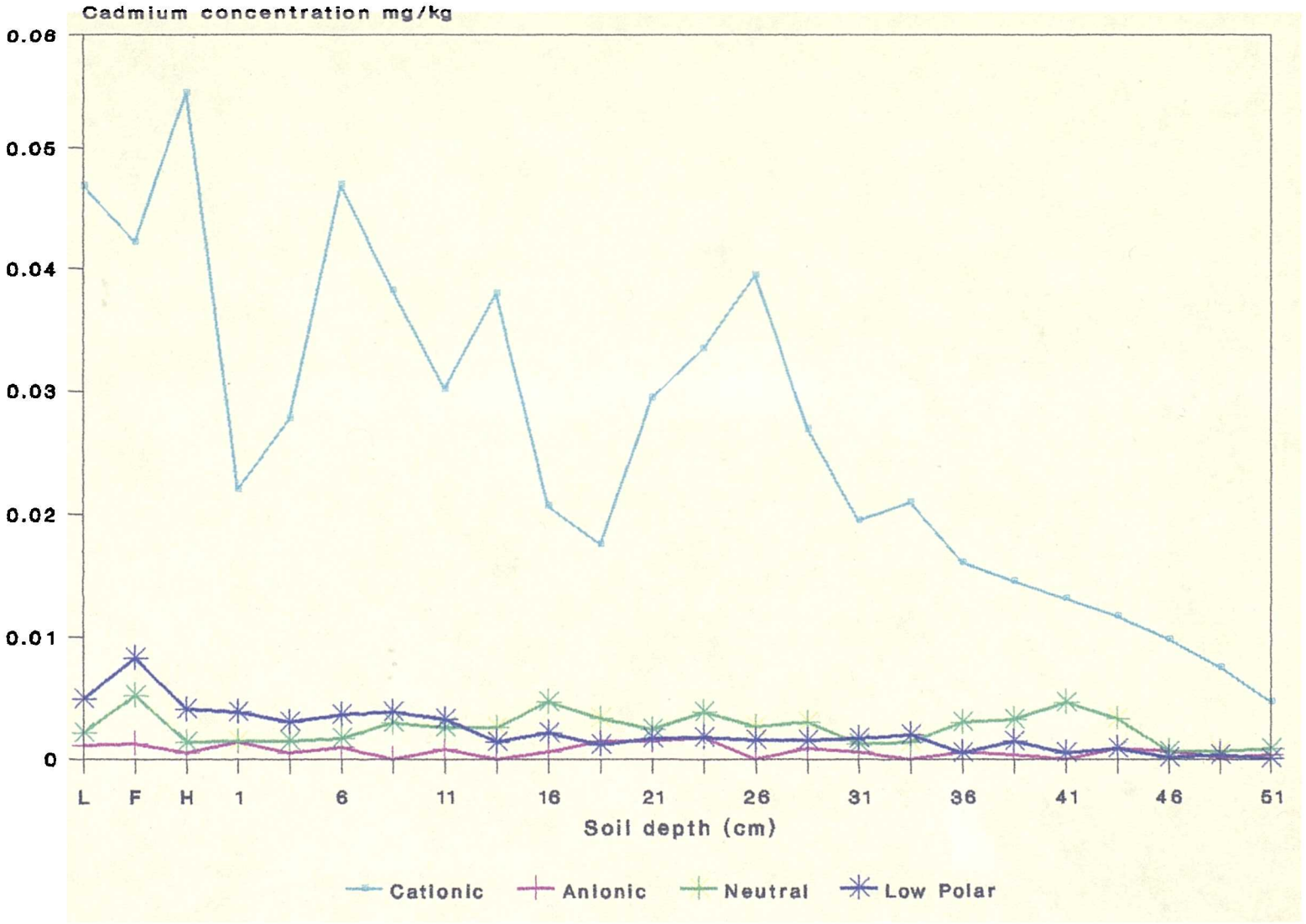


**Fig.4.4.4c Cadmium speciation of water extracts of Hallen Wood (1987) soil.**

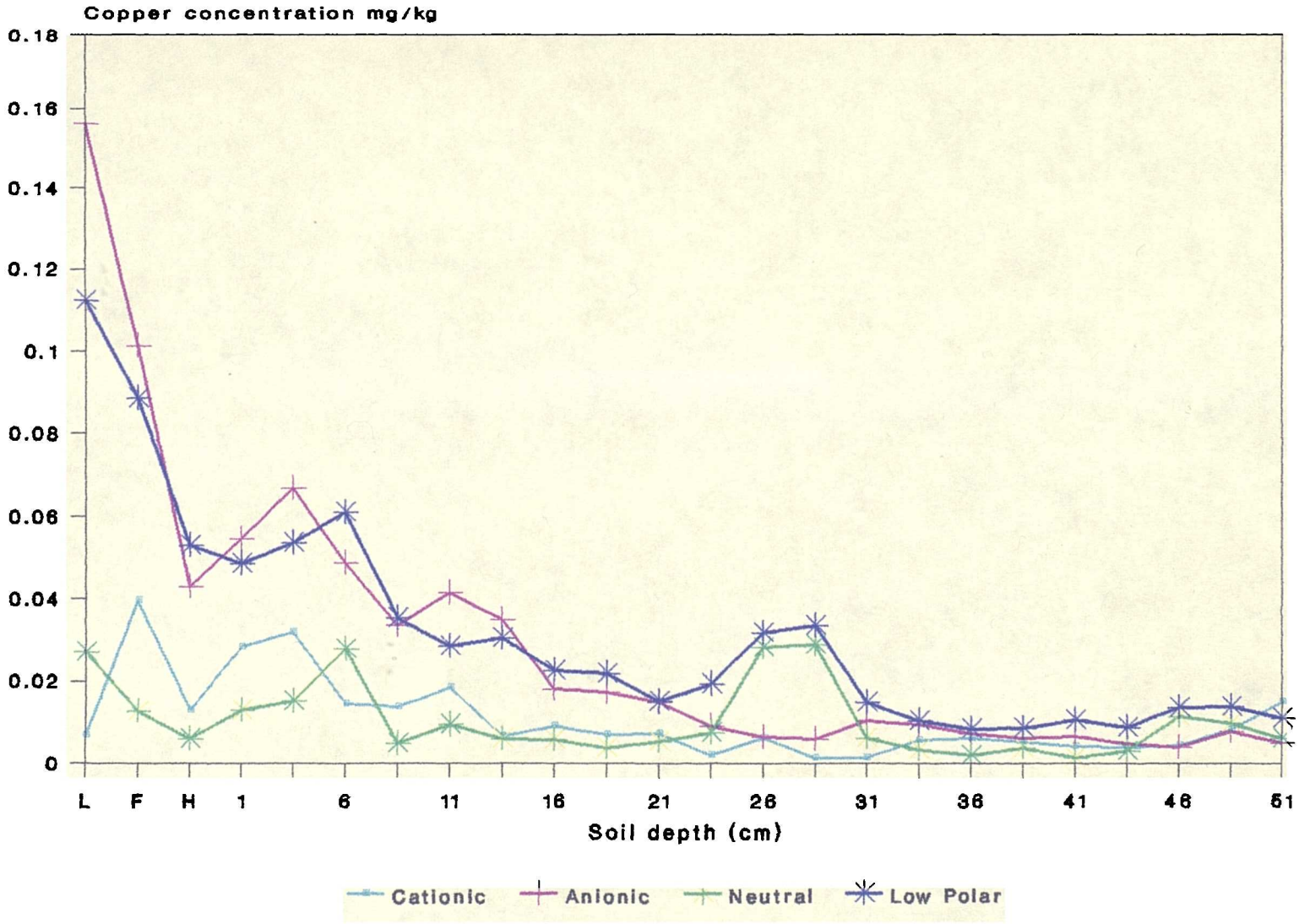


**Fig.4.4.4d Copper speciation in water extracts of Hallen Wood (1987) soil.**

a cationic form. The second most important species were neutral and low polar organic forms. Low polar organic forms tended to be more important to 11cm depth, no doubt a result of the surface organic matter producing an abundance of organic ligands. Otherwise neutral species were more abundant at depth apart from at 31-36cm depth where low polar species again were more important - possibly related to the higher content of organic matter at this point in the profile. The most important Pb species in the Hallen profile were cationic forms; but unlike Cd and Zn, the Pb cationic forms only dominated in the top 13.5cm and at the base of the profile (to 51cm depth). Low polar organic forms took on the second most important role to a depth of 36cm (c.f. Cd and Zn) after which neutral species assumed secondary importance at depth. Anionic species were much more important for Pb than they were for Zn and especially Cd. However, Cu was totally different to its heavy metal compatriots. The most important Cu species were low polar organic and anionic forms. Low polar organic Cu forms were dominant throughout the profile to 51cm depth. After 21cm depth anionic Cu declined in importance. Cationic Cu was the third most important Cu form in solution. The sequence of species importance therefore followed the order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd | : | Cationic | » | Neutral | = | Low Polar | > Anionic |
| Zn | : | Cationic | » | Neutral | = | Low Polar | > Anionic |
| Pb | : | Cationic | > | Low polar | ≥ | Neutral | > Anionic |
| Cu | : | Low Polar | ≥ | Anionic | > | Cationic | ≥ Neutral |

The solution composition of Cd and Zn species indicates that these two metals were relatively immutable to any variation in the soil composition, soil pH and any changes in solution variables that were associated with the Hallen profile. The similarity in the species composition of these two metals was remarkably close, although there was a hint that the predominance of Zn cationic species at depth was not quite as great as Cd cationic forms. The species composition of Cu down the profile appeared to be a little more mutable. For although low polar Cu remained fairly constant at 30-50%, cationic and neutral forms tended to increase at depth below 21cm at the expense of anionic forms. Not too much should be read into the sharp increase in neutral forms at 23.5-28.5cm depth at the expense of anionic forms. This swift departure from the general trends of the two species suggests that some mistake in the analytical proceedings may have occurred at this point. Pb, however, is perhaps the most changeable in its species composition. Although Pb cationic forms were the principal species, their abundance was markedly reduced in the mid-range of the Hallen profile to 51cm depth.

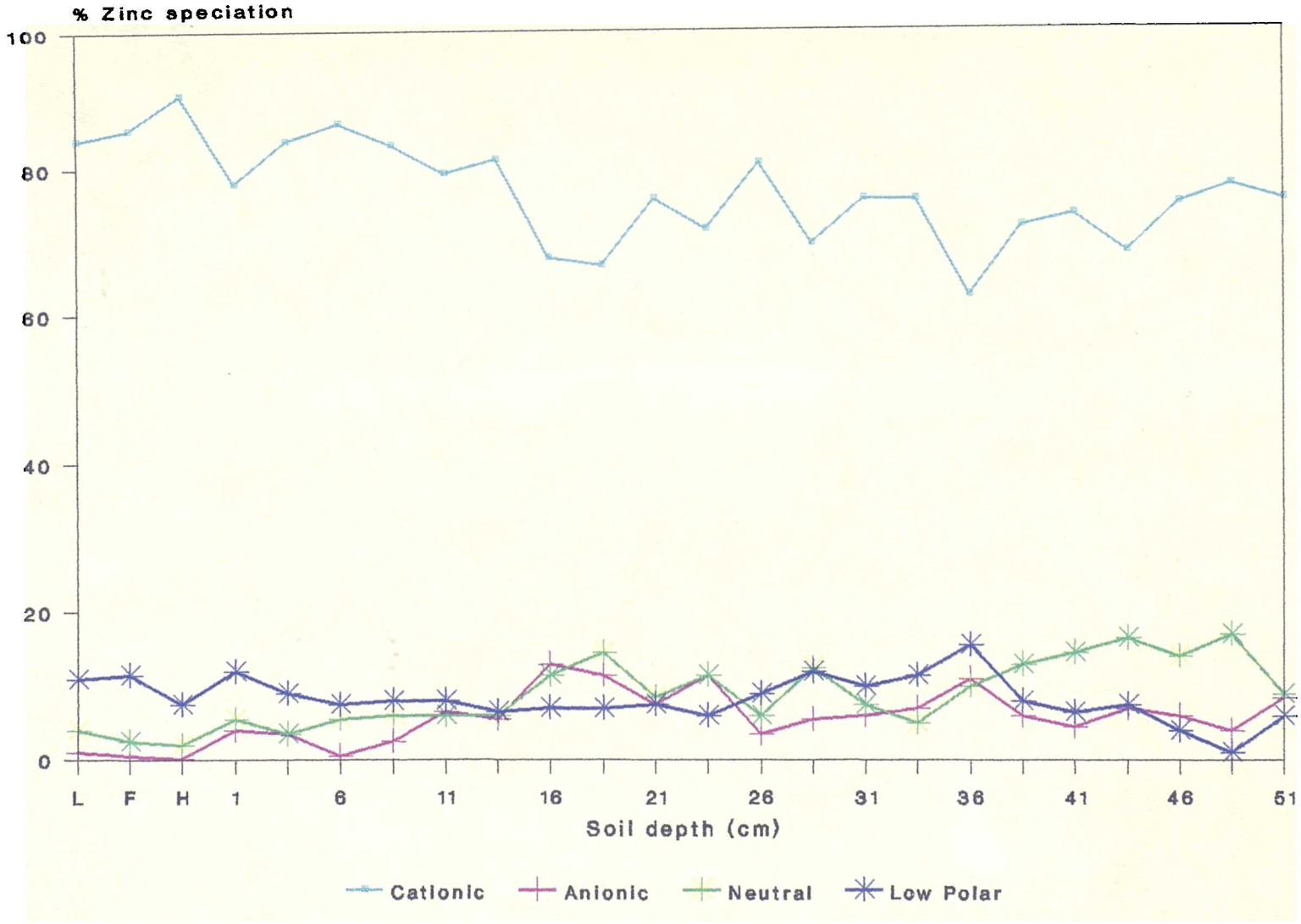


**Fig.4.4.5a % Zinc speciation in water extracts of Hallen Wood (1987) soil.**

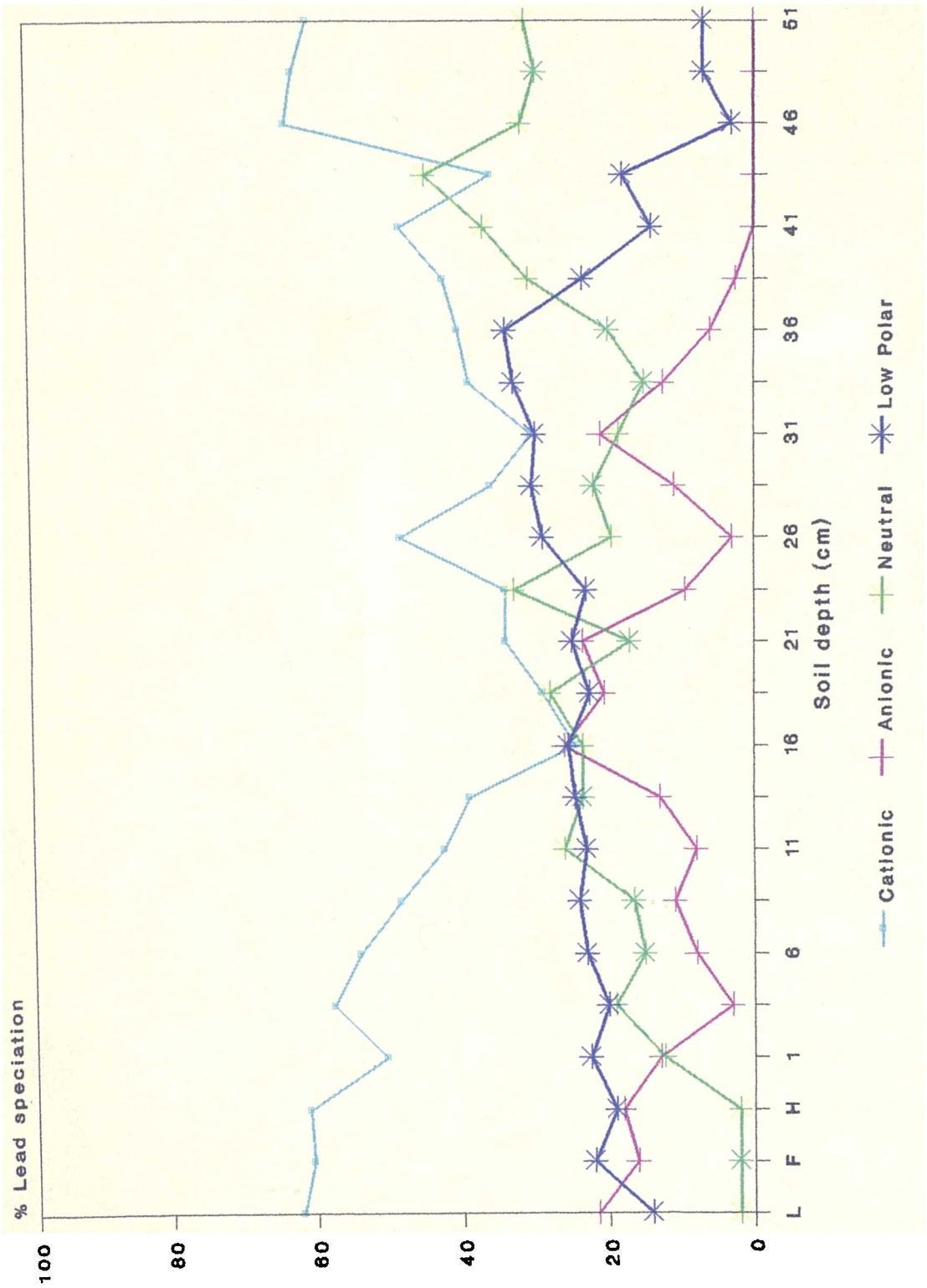


**Fig.4.4.5b % Lead speciation in water extracts of Hallen Wood (1987) soil.**

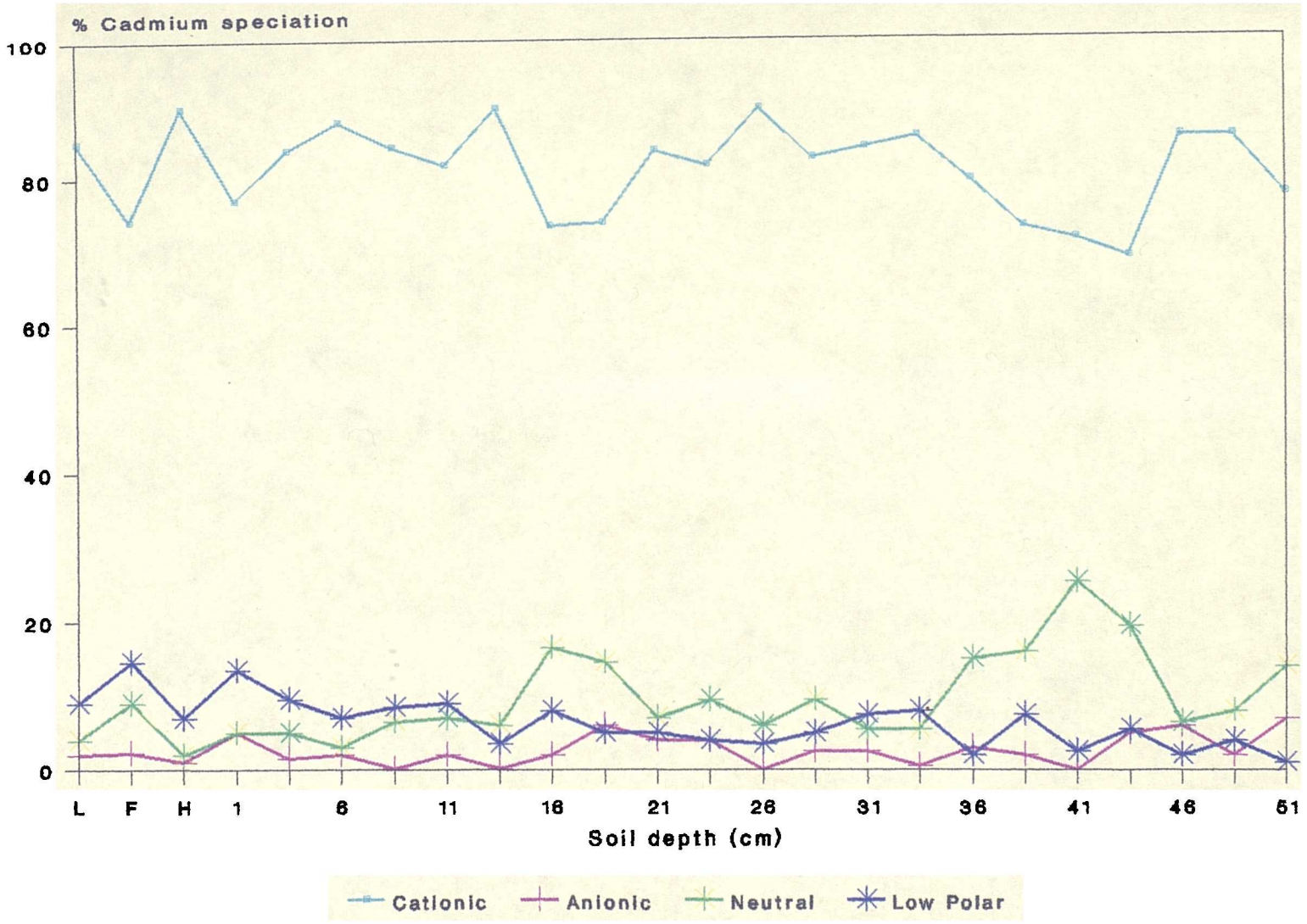


Fig.4.4.5c % Cadmium speciation in water extracts of Hallen Wood (1987) soil.

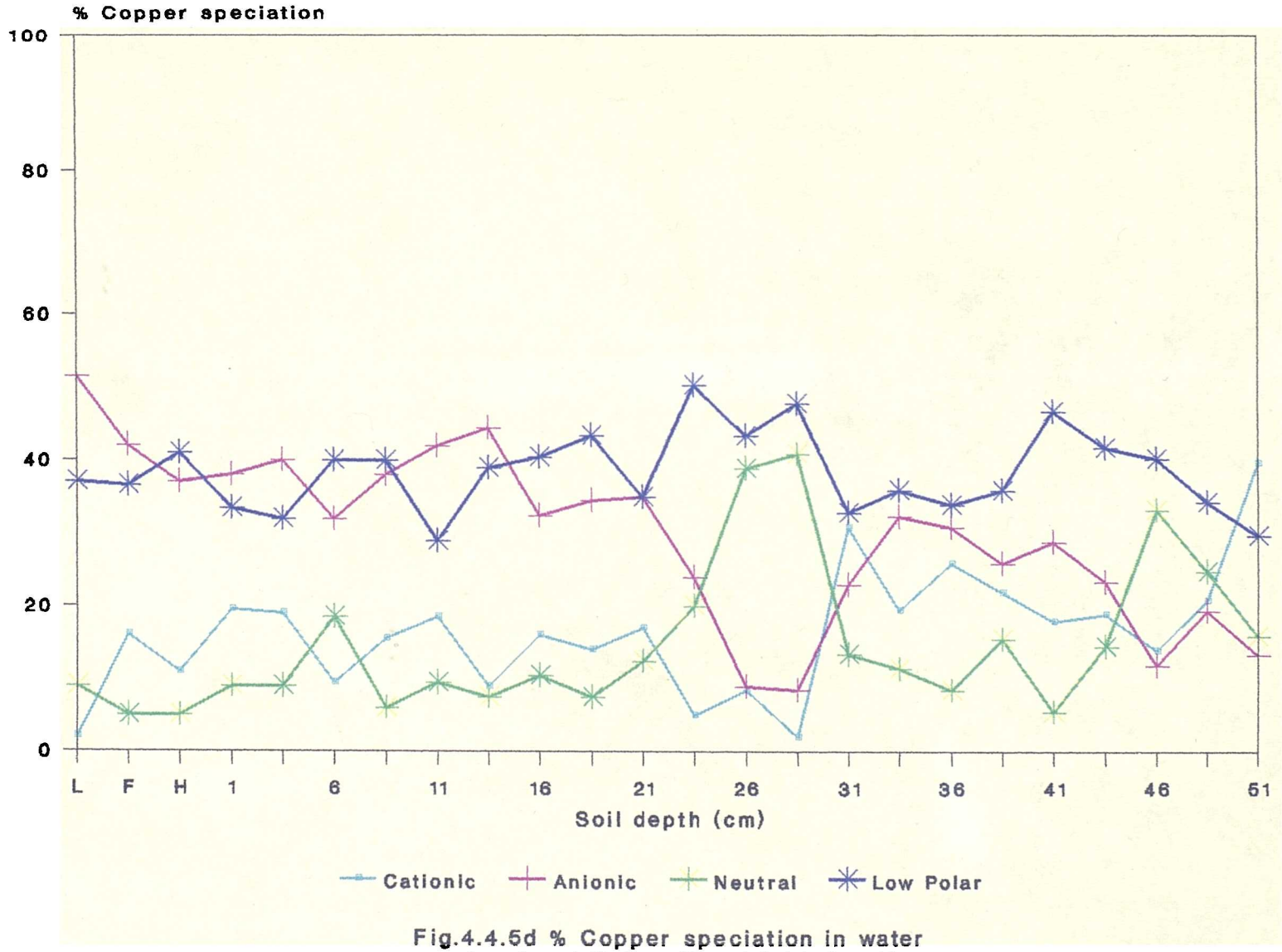


Fig.4.4.5d % Copper speciation in water extracts of Hallen Wood (1987) soil.

The overall analytical precision of heavy metal determinations in solutions can be established from the average of the standard deviations calculated from a representative number of samples analysed (Tramontano *et al.*1987). For the total metal concentrations found in both woodlands, the average overall precision (where $n \geq 30$) was $< \pm 15\%$ where Cd was $\pm 10\%$, Zn was $\pm 12.5\%$, Cu was $\pm 13\%$ and Pb was $\pm 15\%$. The precision for the principal species of Cd and Zn was also good as it reflected their overall total metal concentrations: Cd $\pm 10.5\%$ (cationic) and Zn $\pm 14\%$ (cationic). Species that were not quite so overwhelmingly predominant (to the degree that the Cd and Zn cationic species were) were determined at lower analytical concentrations and hence the precision was somewhat poorer at 20-25% e.g. Cu low polar and anionic species, and Pb low polar and neutral species. Some species such as Pb cationic species had a precision of $\pm 20\%$ in Hallen Wood and a very poor precision in Haw Wood. Poor precision of species such as cationic Pb in Haw Wood and Cd anionic species was a result of low analytically recorded values verging on or at the detection limit.

The percentage recovery of metals is illustrated in Fig.4.4.6 for Hallen Wood. In general the optimal % recovery of metals followed the order:

$$Zn, Cd > Cu > Pb$$

Zn and Cd recovery were mainly within $\pm 10\%$ of 100% which was reasonably satisfactory considering the low metal concentrations being dealt with. The average Cd recovery was $99.97 \pm 7.78\%$, whereas for Zn it was $97.52 \pm 5.77\%$. Cu recovery was also fairly good although there was a tendency for negative bias. Its mean % recovery was $95.56 \pm 7.65\%$. However, Pb did not have such a good % recovery and was much more variable - it had a mean recovery of $118.42 \pm 26.88\%$. This perhaps indicates the apparent succeptibility of Pb to interference effects when measured by GFAAS.

Fig.4.4.7 shows data that have been obtained from neutral salt extraction with 0.1M $NH_4NO_3$. This system of extraction is totally different to that of deionised water in that it is totally dominated by ammonium and nitrate ions, and also the pH of the resultant solution is far lower. The extraction (1:4 soil: solution ratio) was sequentially carried out after a deionised water extraction to initially remove the water soluble metals. In a nitrate dominated system one might expect the speciation of metals to take on a dominant cationic form. So in a simple water system that contains dissolved metals of their nitrate

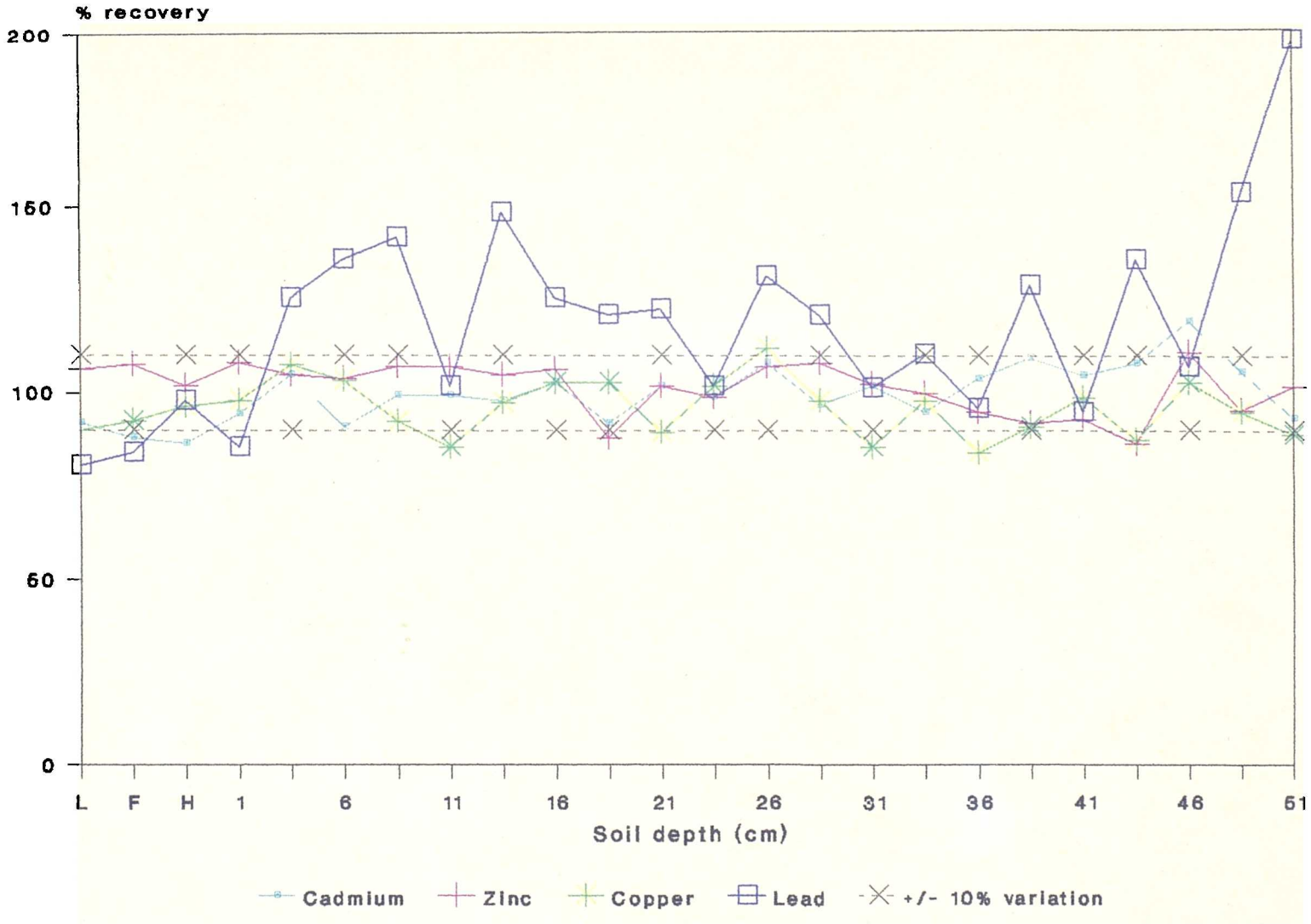


**Fig.4.4.6 % Recovery of metals in water extracts of Hallen Wood (1987) soil.**

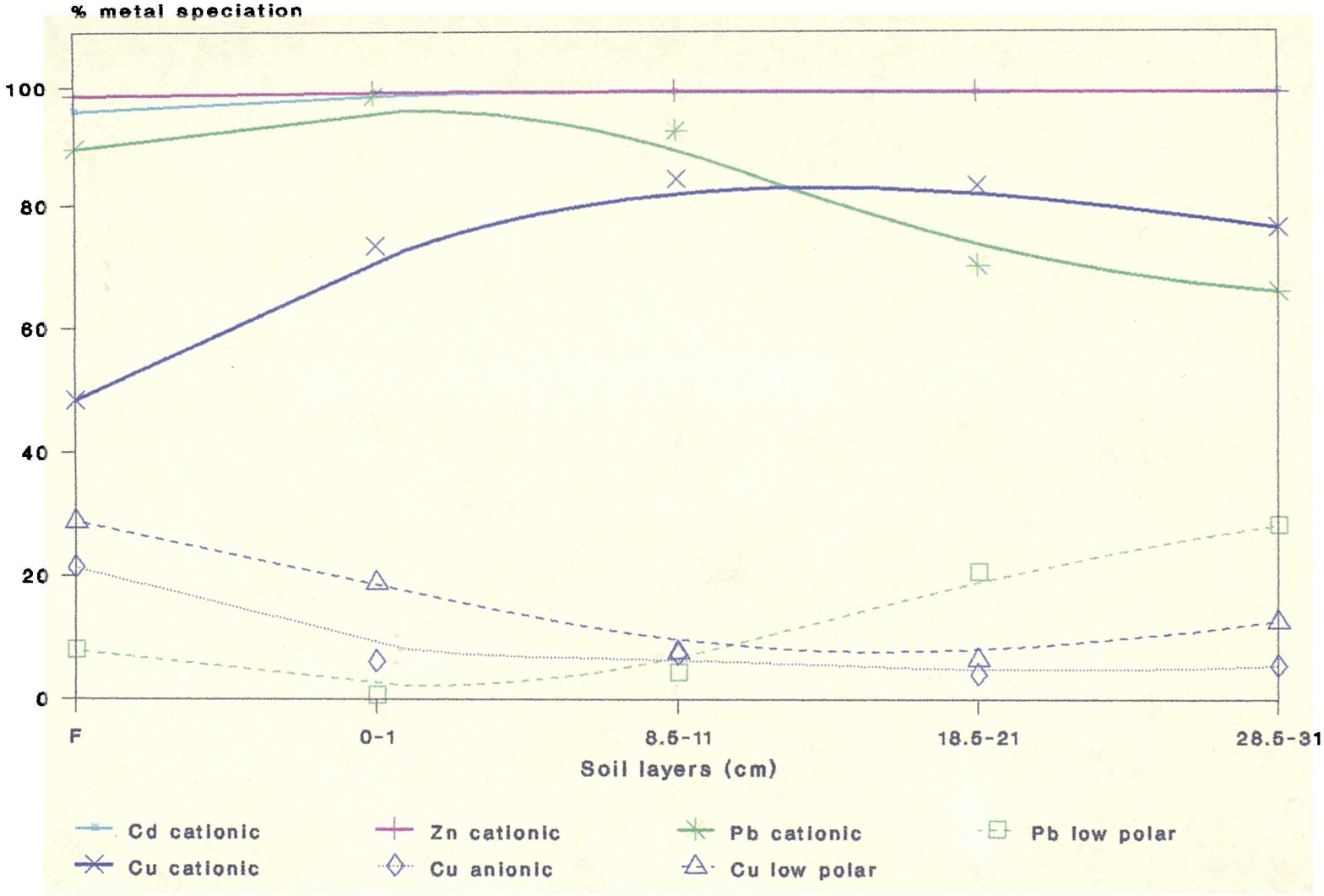


**Fig.4.4.7 % speciation of metals extracted from Hallen Wood soil by 0.1M Ammonium nitrate.**

## Table 4.4.3 % Speciation of Heavy Metals Dissolved as Nitrate Salts in a Water System

| Element | Total µg/ml | % Cationic | % Anionic | % Neutral | % Low Polar |
|---|---|---|---|---|---|
| Cd | 0.666 | 98.33 | 0.17 | 0.17 | 1.34 |
| Cu | 0.534 | 98.22 | 0.16 | 0.40 | 1.23 |
| Pb | 0.273 | 97.10 | 0.41 | 1.24 | 1.24 |
| Zn | 0.710 | 97.84 | 0.15 | 0.77 | 1.23 |

---

salts results such as those in Table 4.4.3 might be expected. In Hallen Wood soil 0.1M $NH_4NO_3$ extracts, a greater variety and abundance of ligands will be available to form complexes with the free metal ions. In Fig.4.4.7 Cd and Zn were predominantly cationic in form. Pb and Cu were also highly cationic in form but not to the same degree as Cd and Zn. The fact that the metals were mainly cationic perhaps indicates the displacement of metals principally from negative charged surface sites by the ammonium ion, probably in the main from clay mineral surfaces (in mineral soil). Despite any shortcomings, the system helps to demonstrate how much more important low polar and anionic ligands are in influencing the speciation of Pb and Cu.

An interesting feature of the data collected in Table 4.4.3 and Fig.4.4.7 is that although the metal concentrations in solution were much higher, the % recovery of metals tended to be nearer 90% rather than 100%. This may mean that higher solution concentrations were subject to adsorption effects. However, it may be that the speciation procedure for lower concentration solutions was prone to minor interference effects whether the metal was measured by GFAAS (e.g. Cd) or by FAAS (e.g. Zn).

## 4.4.4. Correlation Coefficients of Heavy Metal Species with Various Soil Variables in Hallen Wood Soil

Cationic, anionic, neutral, low polar and total water soluble heavy metal species have been correlated against numerous soil variables that have been outlined in Chapter 3, Section 6.3. Water soluble variables have also been included (i.e. soluble $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$, $Fe^{2+}$, $Mn^{2+}$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$). The same conditions apply as in Chapter 3 except that n = 20. Again correlations of ±0.800 or greater will be considered with a confidence limit of $p < 0.1\%$.

**Table 4.4.4**

| | | Total Water Soluble | | | |
|---|---|---|---|---|---|
| | | Cd | Pb | Zn | Cu |
| Exchangeable | Mg | -0.872 | -0.862 | -0.850 | - |
| Exchangeable | Ca | -0.854 | -0.808 | -0.788 | - |
| Exchangeable | Al | 0.829 | 0.861 | 0.829 | - |
| Total | Ca | -0.862 | -0.853 | -0.860 | - |
| Exchangeable | Fe | - | - | - | 0.839 |
| Exchangeable | Pb | - | - | - | 0.804 |
| Total | Pb | - | - | - | 0.858 |

---

Total water soluble metals have been considered in Section 4.3 and so little more need be said except for the fact that of the total soil and exchangeable metal concentration variables that appeared to relate best to soluble Cd, Pb and Zn were calcium and magnesium (Table 4.4.4).

Whatever the interpretation of Table 4.4.4, it is clear that the distributions of soluble Cd, Pb and Zn were different to that of Cu and hence might suggest that the dominant species for the former three metals might be different to those of Cu. As it is, the coefficients suggest that loss of exchangeable Mg and Ca, and an increase in exchangeable Al are associated with the solubilisation of Cd, Pb and Zn. Interestingly, total soluble metals do not correlate well with their total soil or available metal concentrations. This is perhaps the result of the fact that the latter were more representative of accumulation rather than dissolution processes.

As might be expected the principal species of Cd and Zn (cationic forms) very much reflected the results found for their total soluble metals as both variables correlate with each other very closely: $r = +0.985$ for Cd, $r = +0.980$ for Zn. Cd cationic forms also correlate highly with Zn cationic forms, with $r = + 0.903$. Thus, even within the solution phase of Hallen soil, these two elements demonstrate geochemical similarity.

The principal Cu species also correlate highly with the total soluble Cu: $r = +0.941$ for low polar complexes, $r = +0.930$ for anionic forms. As with total soluble Cu, these two species forms also correlate highly with water soluble aluminium, $r = +0.882$. However, Pb was somewhat intriguing; although it's cationic species were the predominant species form, its two subdominant forms (low polar and neutral forms) correlate more closely with

total soluble lead. The coefficient values for total soluble Pb decrease in the order:

| | | | | |
|---|---|---|---|---|
| r = | +0.924 | > | +0.902 | > +0.855 |
| | low polar complexes | | neutral forms | cationic forms |

This perhaps signifies the importance of organic ligands, especially in the complexation of Pb in the Hallen soil profile. Another interesting feature about Pb species in the profile is that Pb cationic forms appear to relate closely to Cu species:

| | | | | |
|---|---|---|---|---|
| r = | +0.892 | > | +0.880 | > +0.873 |
| | total soluble copper | | low polar copper complexes | copper anionic forms |

In addition, Pb low polar complexes are also closely related to total available Cu, r = +0.870. The close ties that Pb appeared to have with Cu might suggest that dissolved organic carbon and humic substances within the profiles influence Pb to some degree in its soluble state.

### 4.4.5. Analytical Heavy Metal Speciation Results for Haw Wood Soils

Speciation of metals in Haw soil was carried out only in the topsoil which included the L/F/H layer and 1-11cm depth in the mineral soil. Fig.4.4.8 shows that yet again, soluble Cd and Zn were dominated by cationic species. Again, Cu was dominated by low polar organic and anionic species, but in Haw soil anionic forms were clearly much more important than they were in Hallen soil. Although cationic Pb was important in the L/F/H layer, low polar organic / neutral forms were perhaps the most important species in the mineral soil.

Fig.4.4.9 provides a clearer illustration of how the metal species in solution are distributed proportionally. Obviously Cd and Zn were still very much dominated by cationic species, although not to the same degree as in Hallen Wood. Their cationic species also showed a decline with depth resulting in an increase of other species. This may be as a result of the gradient in pH that Haw soil has in the surface topsoil, ranging from about pH5.0 in the litter layers to pH6.0 at 11cm depth. Neutral and low polar species were the second most abundant species, with neutral species tending to predominate over low

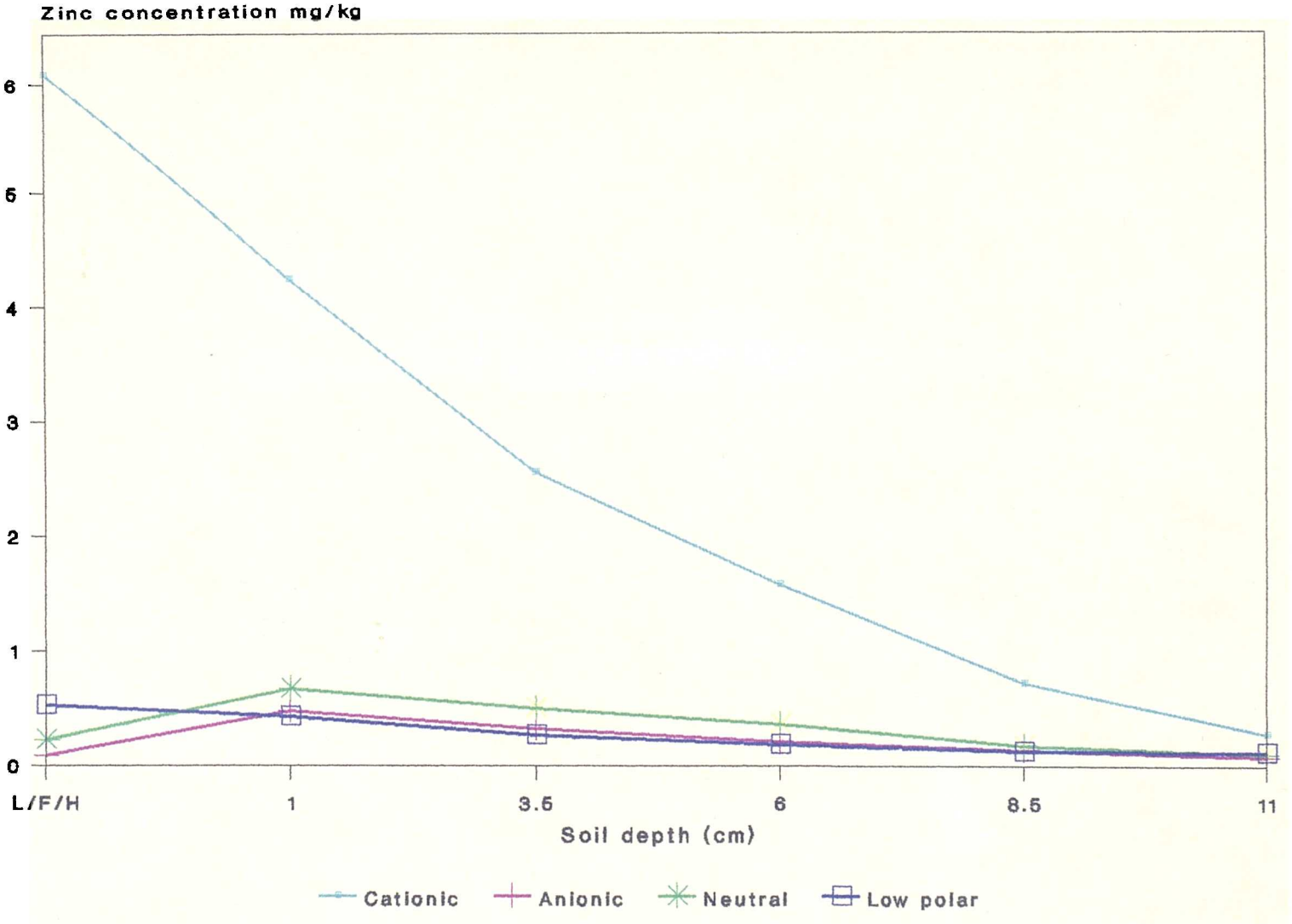


**Fig.4.4.8a Zinc speciation of water extracts from Haw Wood (1987) soil.**

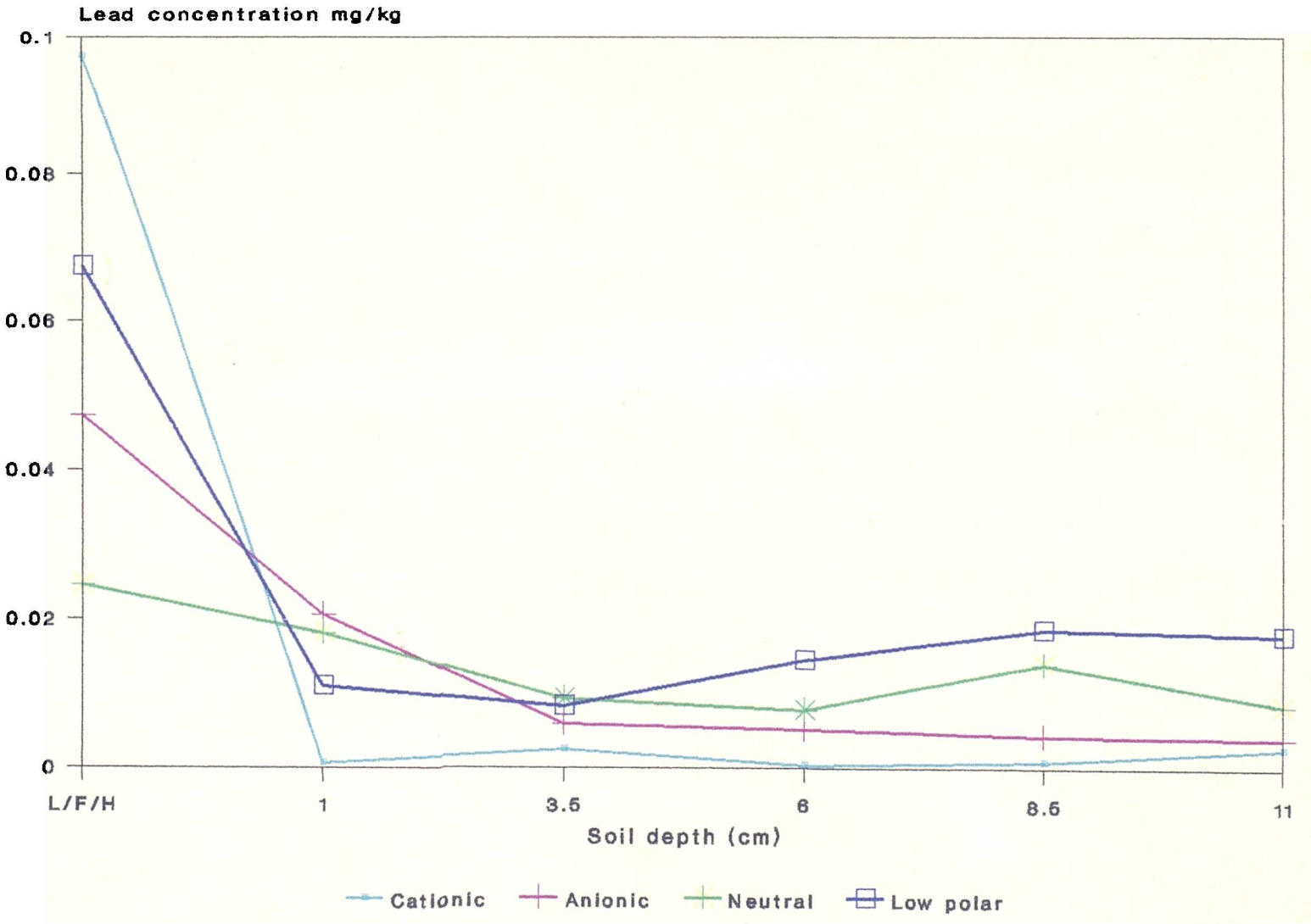


**Fig.4.4.8b Lead speciation of water extracts from Haw Wood (1987) soil.**

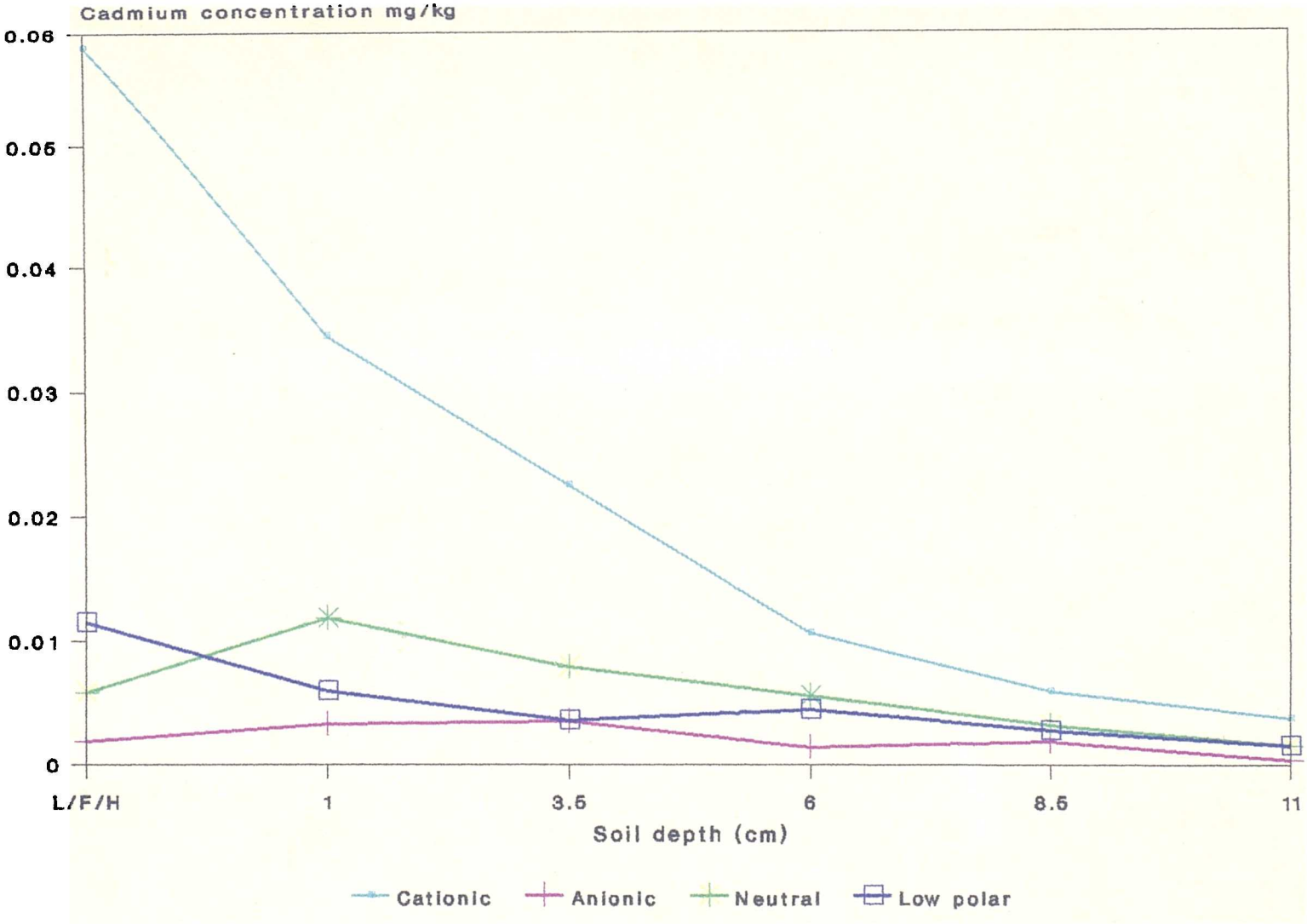


**Fig.4.4.8c Cadmium speciation of water extracts from Haw Wood (1987) soil.**

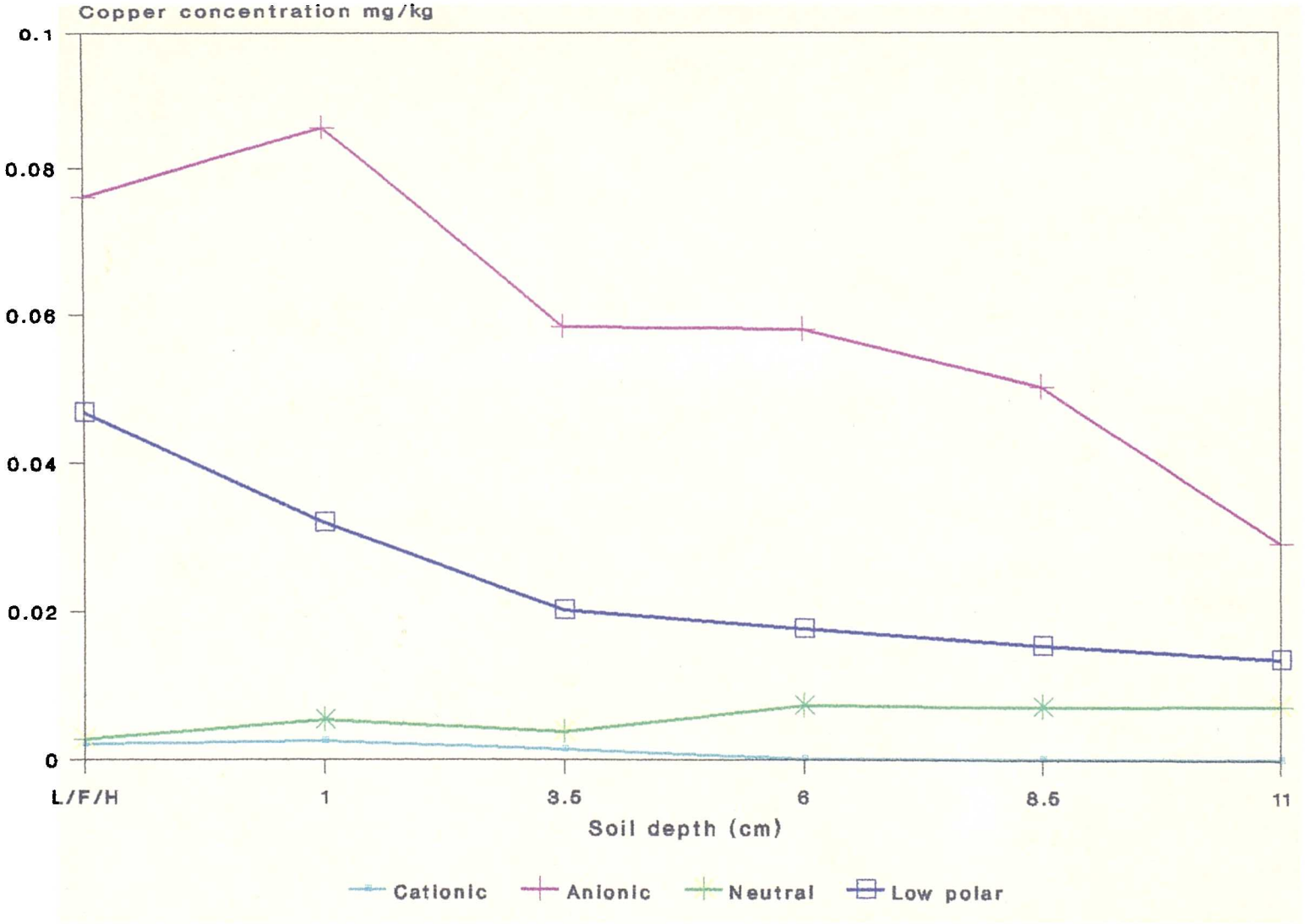


**Fig.4.4.8d Copper speciation of water extracts from Haw Wood (1987) soil.**

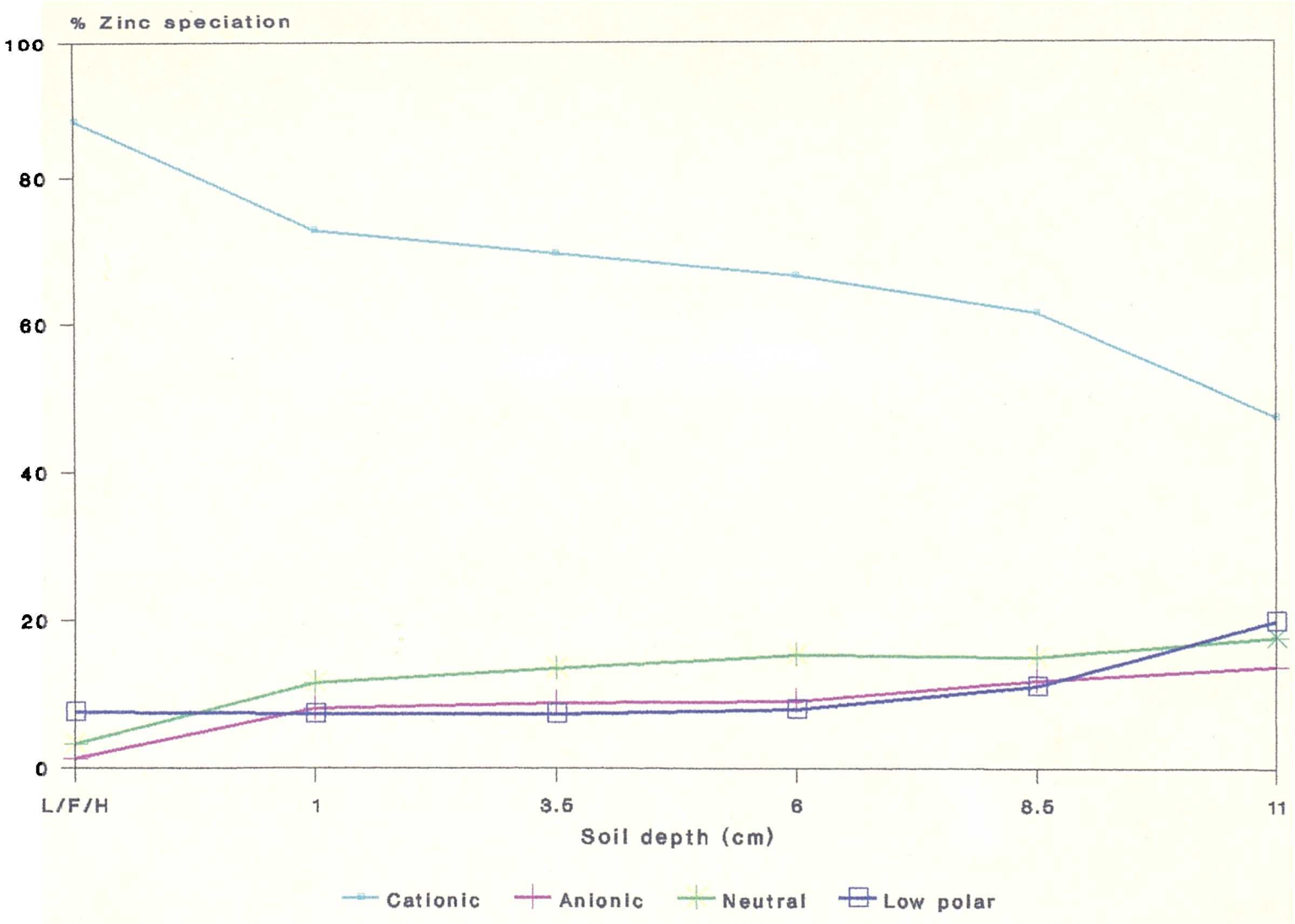


**Fig.4.4.9a % Zinc speciation of water extracts from Haw Wood (1987) soil.**

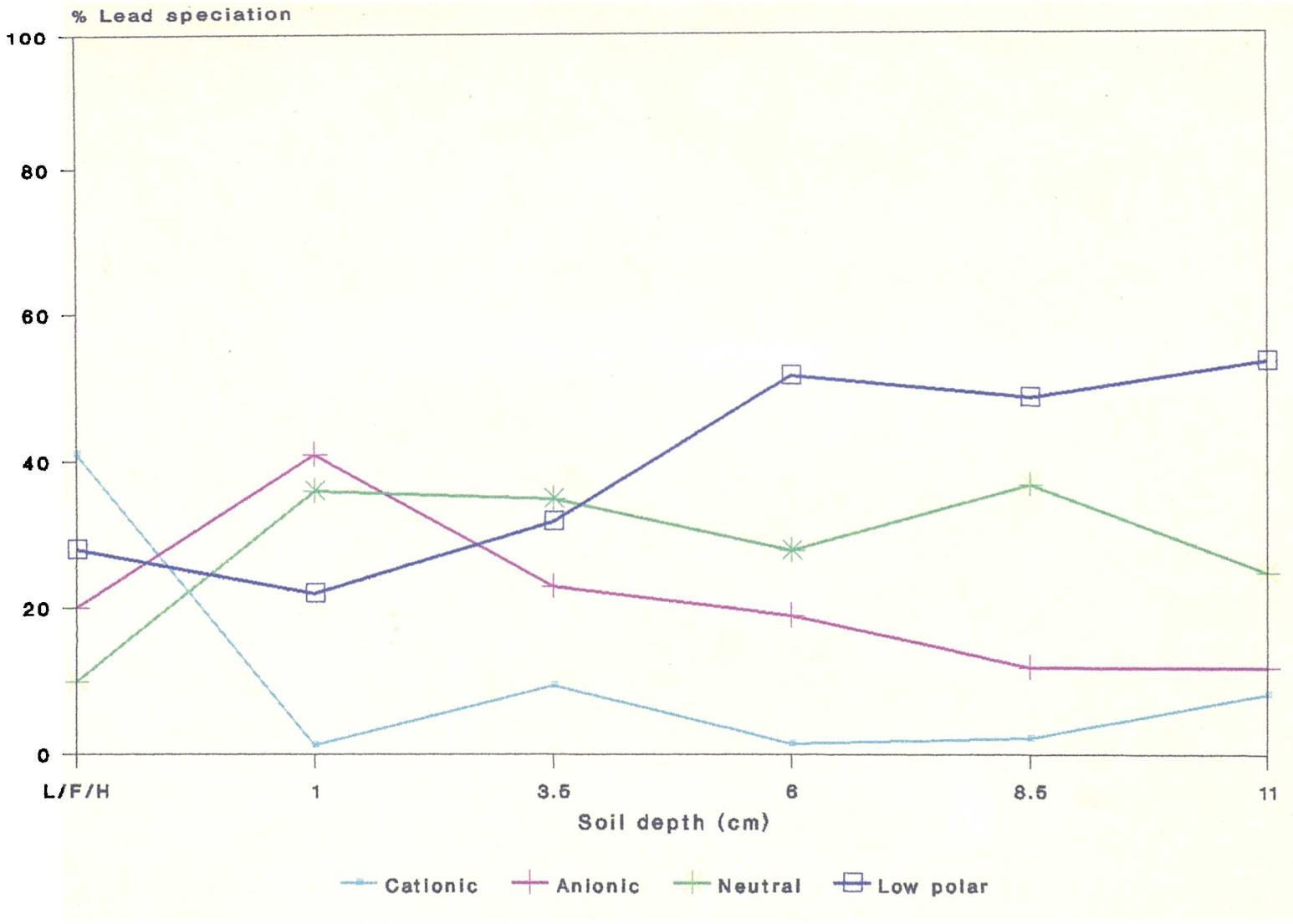


**Fig.4.4.9b % Lead speciation of water extracts from Haw Wood (1987) soil.**

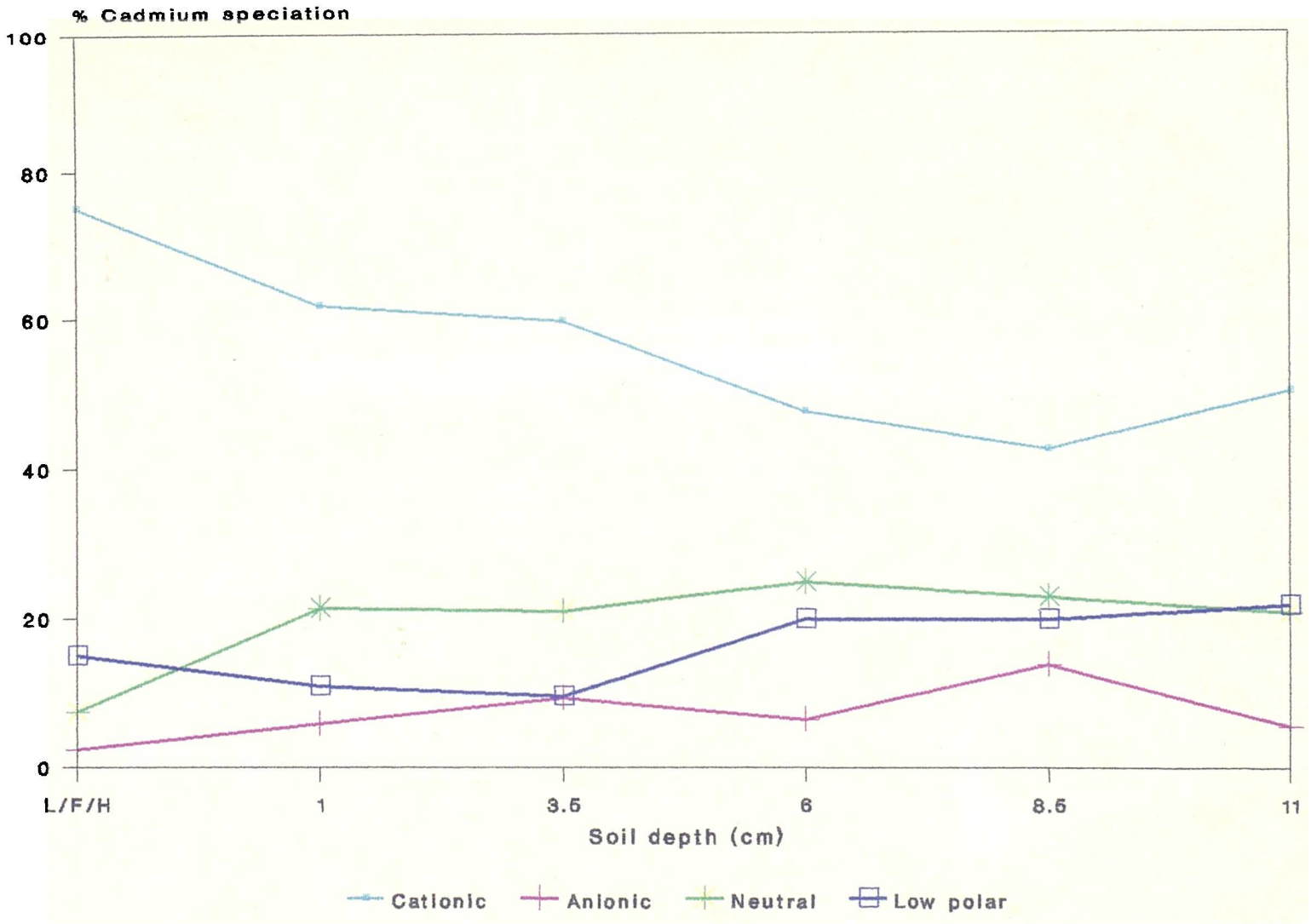


**Fig.4.4.9c % Cadmium speciation of water extracts from Haw Wood (1987) soil.**

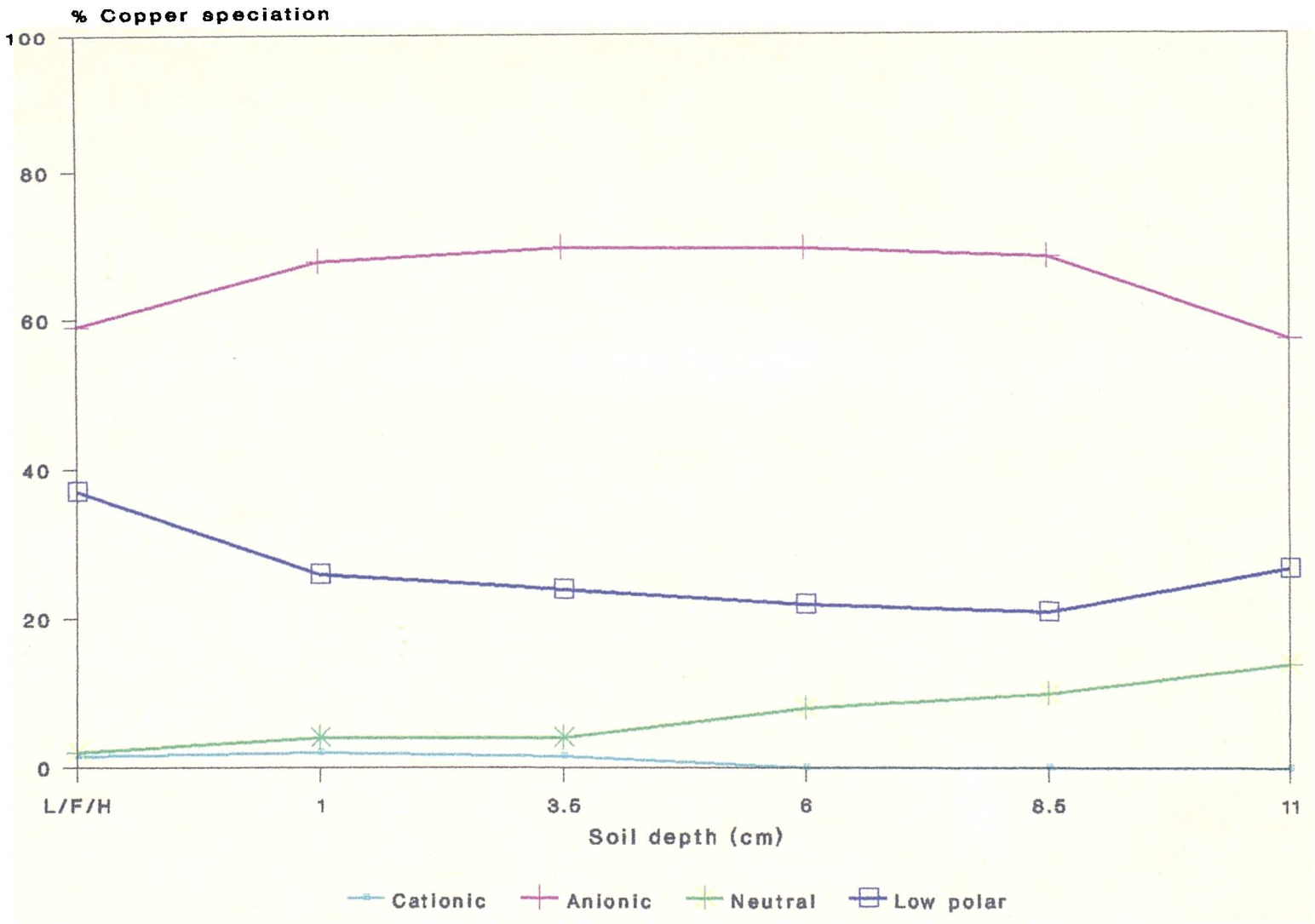


**Fig.4.4.9d % Copper speciation of water extracts from Haw Wood (1987) soil.**

polar complexes. Perhaps the most interesting comparison between the Cd and Zn species was the greater abundance of Zn cationic species in relation to Cd cationic species. This might possibly be as a result of the effect of organic matter in the Haw topsoil which appears to have a greater effect on Cd solubility than on Zn solubility (see Section 4.3.2).

In relation to Hallen Wood, the composition of Haw Pb species was very much different. In particular, Pb low polar and neutral species dominated at the expense of cationic species. Only within the L/F/H layer were Pb cationic species of great significance. Pb low polar organics appeared to be of greatest importance in the Haw topsoil. However, anionic and low polar species were still the dominant species for Cu. Nevertheless, Cu anionic species were far more abundant in the Haw profile than they were in the Hallen profile. Cu low polar complexes were clearly subdominant to anionic forms. The other feature of interest was that Cu cationic forms were of a minor but noticeable importance in Hallen Wood, whereas in Haw Wood cationic forms were of little significance. The sequence of species importance for all four metals therefore followed the order:

| | | | | | | |
|---|---|---|---|---|---|---|
| Cd | : Cationic | » | Neutral | ≥ | Low Polar | > Anionic |
| Zn | : Cationic | » | Neutral | ≥ | Low Polar | ≥ Anionic |
| Pb | : Low Polar | > | Neutral | > | Anionic | > Cationic |
| Cu | : Anionic | » | Low Polar | > | Neutral | > Cationic |

Pb species appeared to be the most affected by the conditions prevailing in Haw soil. Cd, Zn and Cu were least affected by soil conditions, although Cd and Zn were perhaps more influenced in their species form as the abundance of cationic species tended to decline with depth.

Fig.4.4.10 illustrates the % recovery of the four metals. The % recovery of Cd, Cu and Zn was fair, but not as good as the recovery in Hallen Wood. The mean recovery for Cd was 93.51±5.69%, for Cu 93.54±3.53% and for Zn 88.98±2.36%. The recovery of Pb has some improvement over that in Hallen Wood, with the mean recovery being 110.43±10.82%.

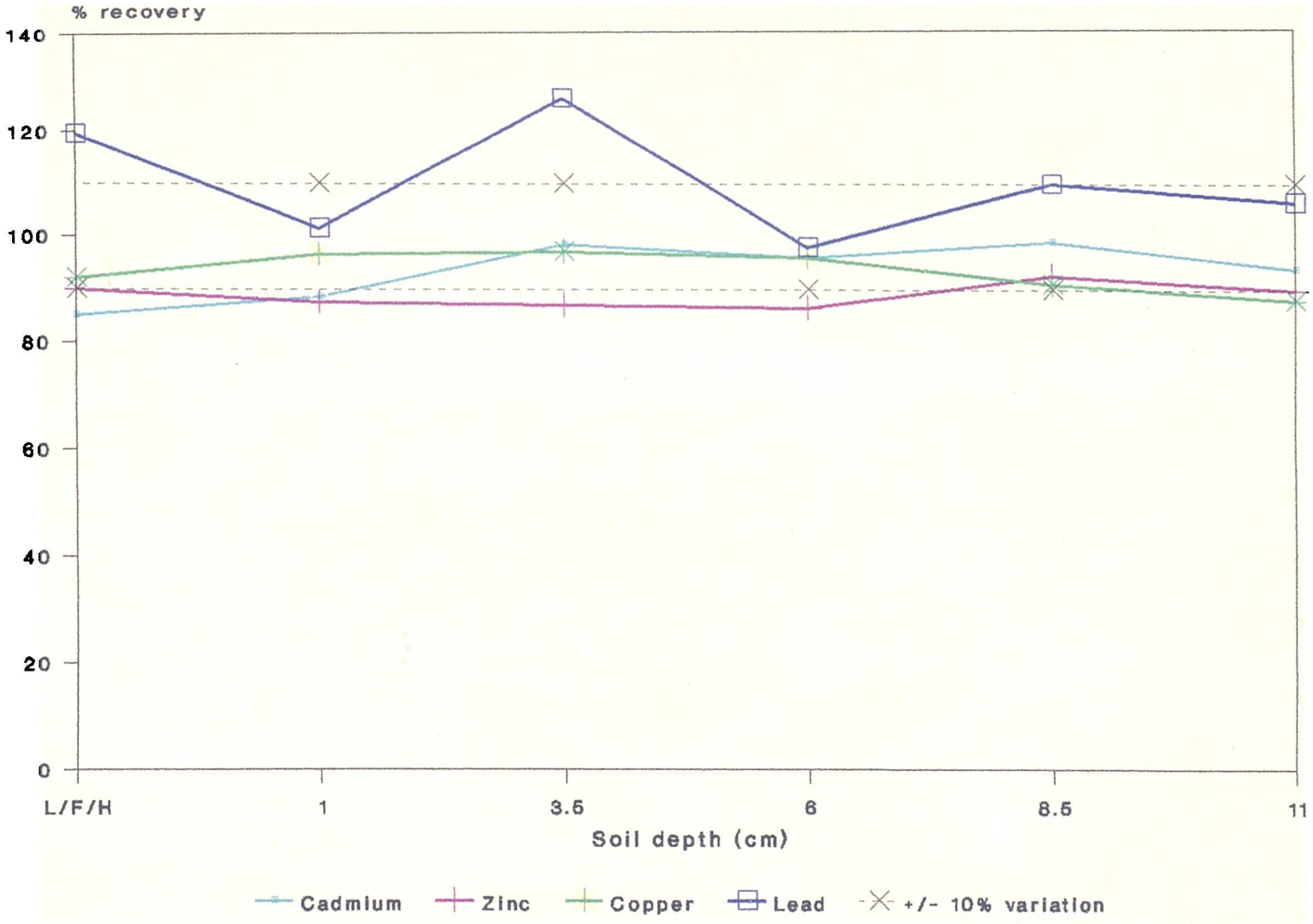


**Fig.4.4.10 % recovery of metals in water extracts from Haw Wood (1987) soil.**

## 4.4.6. Soluble Inorganic Anions and Soluble Metals in Hallen Wood and Haw Wood Soils

Inorganic anion concentrations within the soil solution were obtained as outlined in Section 4.4.1 and Appendix B. The total soluble anion concentrations are illustrated in Fig.4.4.11. Sulphate was the most important anion in terms of concentration (μg/g). Chloride was the next most abundant anion followed by nitrate and phosphate. In terms of equivalents (Fig.4.4.12) chloride dominated the top 11cm and 18.5cm of Haw Wood and Hallen Wood soils respectively. In Haw Wood, chloride and sulphate were both as abundant in the lower section of the profile. In Hallen Wood, however, sulphate becomes the dominant / co-dominant anion between 21-61cm.

In Haw Wood the relationship between soluble anions and cations is illustrated in Table 4.4.5. The most important anion in association with the major cations in solution was the sulphate ion. The chloride ion was also important but does not have as strong an association with sodium as sulphate had. Interestingly all three anions were associated with potassium solubility. Results for Hallen Wood in Table 4.4.6 indicate that all three anions were still associated with potassium solubility. Chloride was very strongly affiliated with sodium in the Hallen profile, whereas nitrate and especially sulphate correlate well with soluble calcium. The sulphate anion is the only anion that correlates with magnesium in solution with any significance (i.e. $r = 0.538$, $p < 1\%$). Sulphate and to a lesser extent nitrate would appear to be accompanying calcium (and to a lesser extent magnesium) down the soil profile. Chloride, however, was associated with the minor elements aluminium, iron and manganese. Results of correlations with heavy metals in the Hallen soil solutions are shown in Table 4.4.7. Again chloride was closest in association with the heavier metals.

The association that sulphate has with calcium is worthy of more attention. They are the only two water soluble variables that are better correlated to pH than any other environmental factor (see Table 4.4.8). Interestingly, the next highest correlations they have with the environmental soil variables are with % base saturation and exchangeable acidity. Metals such as calcium and magnesium are known to be very mobile cations, and soil solutions affected by soil acidification will have increased washout of cations - principally $Ca^{2+}$ and $Mg^{2+}$ (Jacks *et al.*1984). This in effect can lead to the decline of exchangeable cations such as calcium (Billett *et al.* 1990, Ulrich 1983). Correlation coefficients of soluble calcium with other soluble metals are shown in Table 4.4.9 for Hallen Wood. If it is considered that calcium was the most

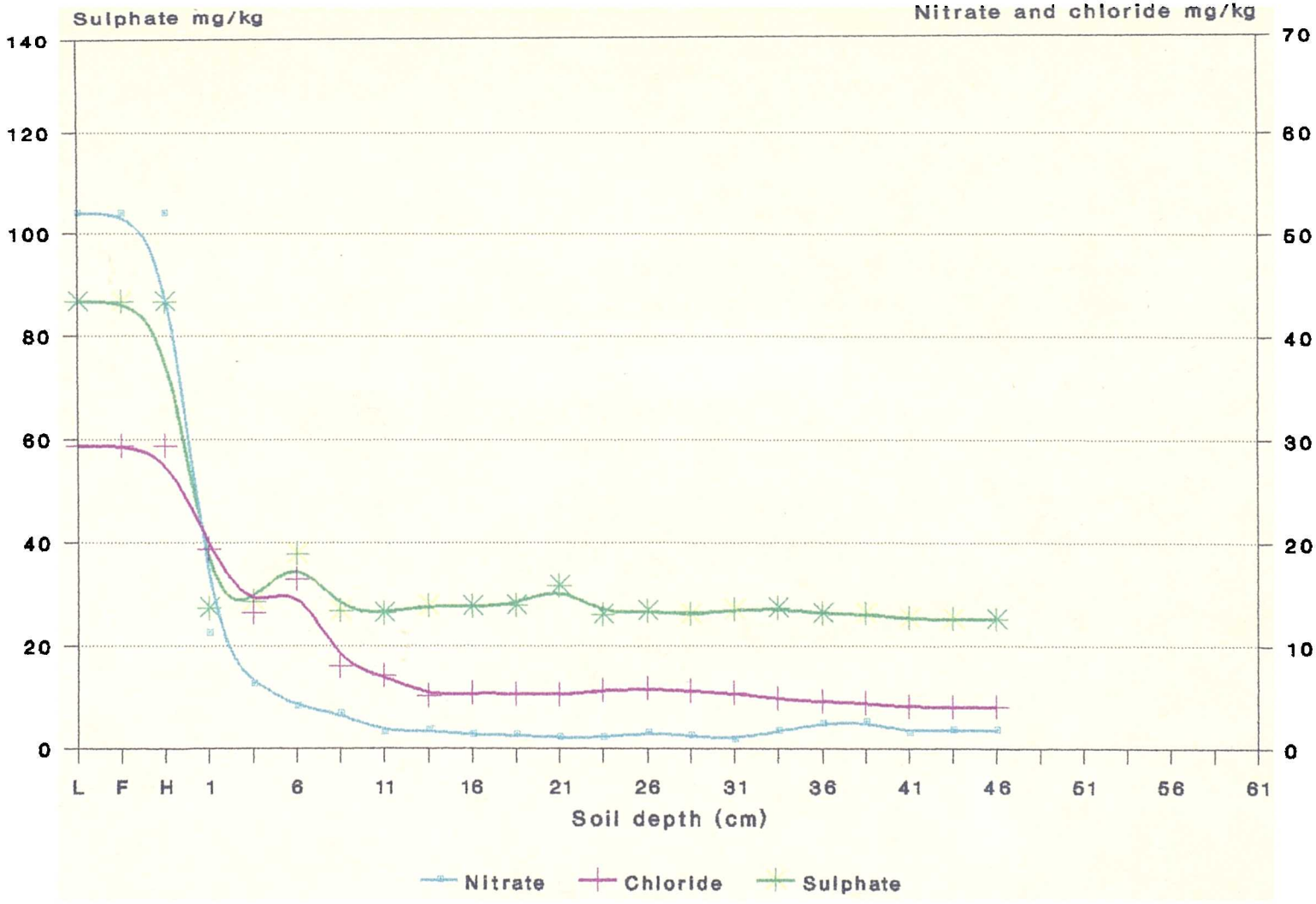


**Fig.4.4.11a Principal anions: chloride, nitrate and sulphate in Haw Wood soil profile 1987 (extracted soil water)**

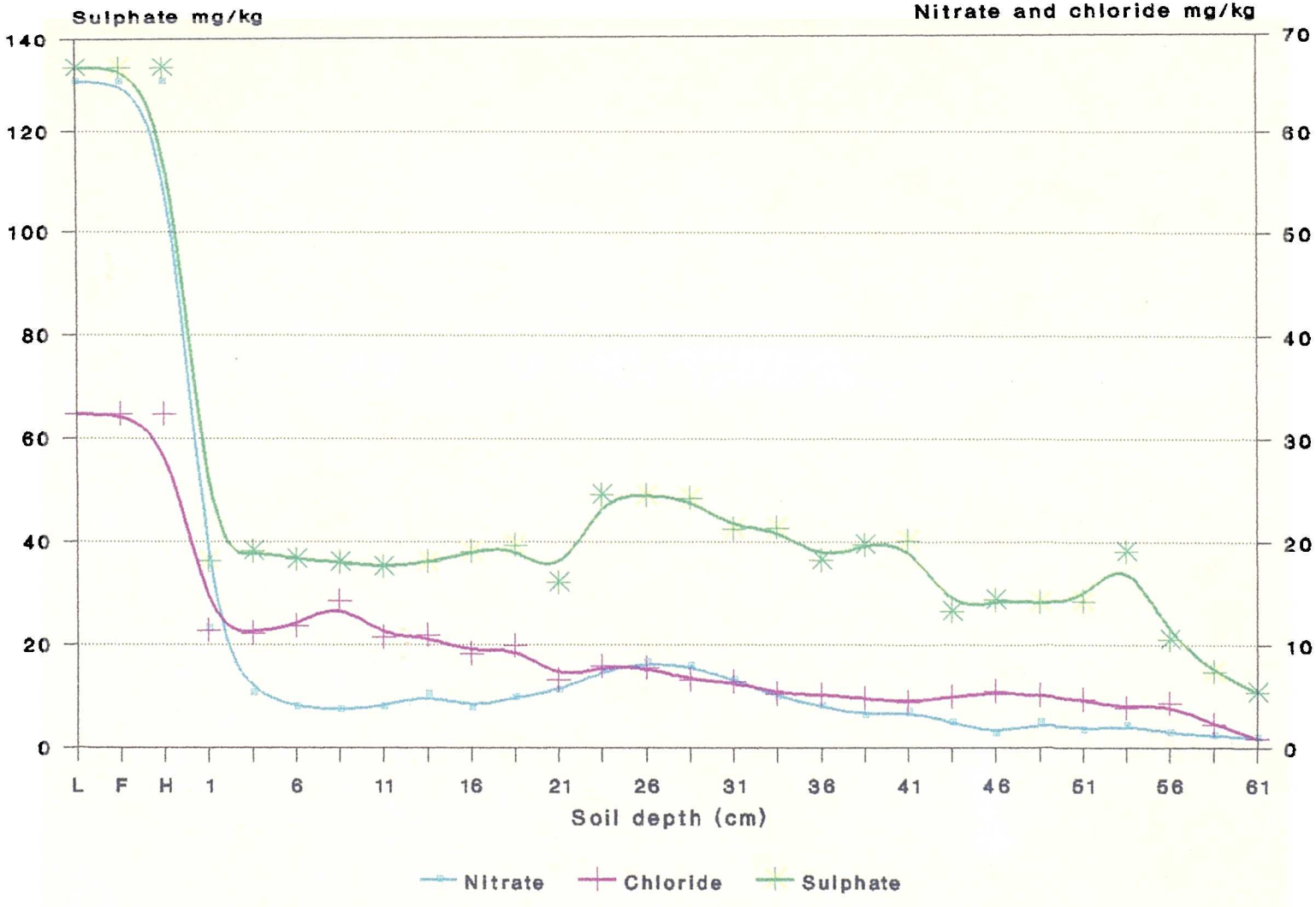


**Fig.4.4.11b Principal anions: chloride, nitrate and sulphate in Hallen Wood soil profile 1987 (extracted soil water)**

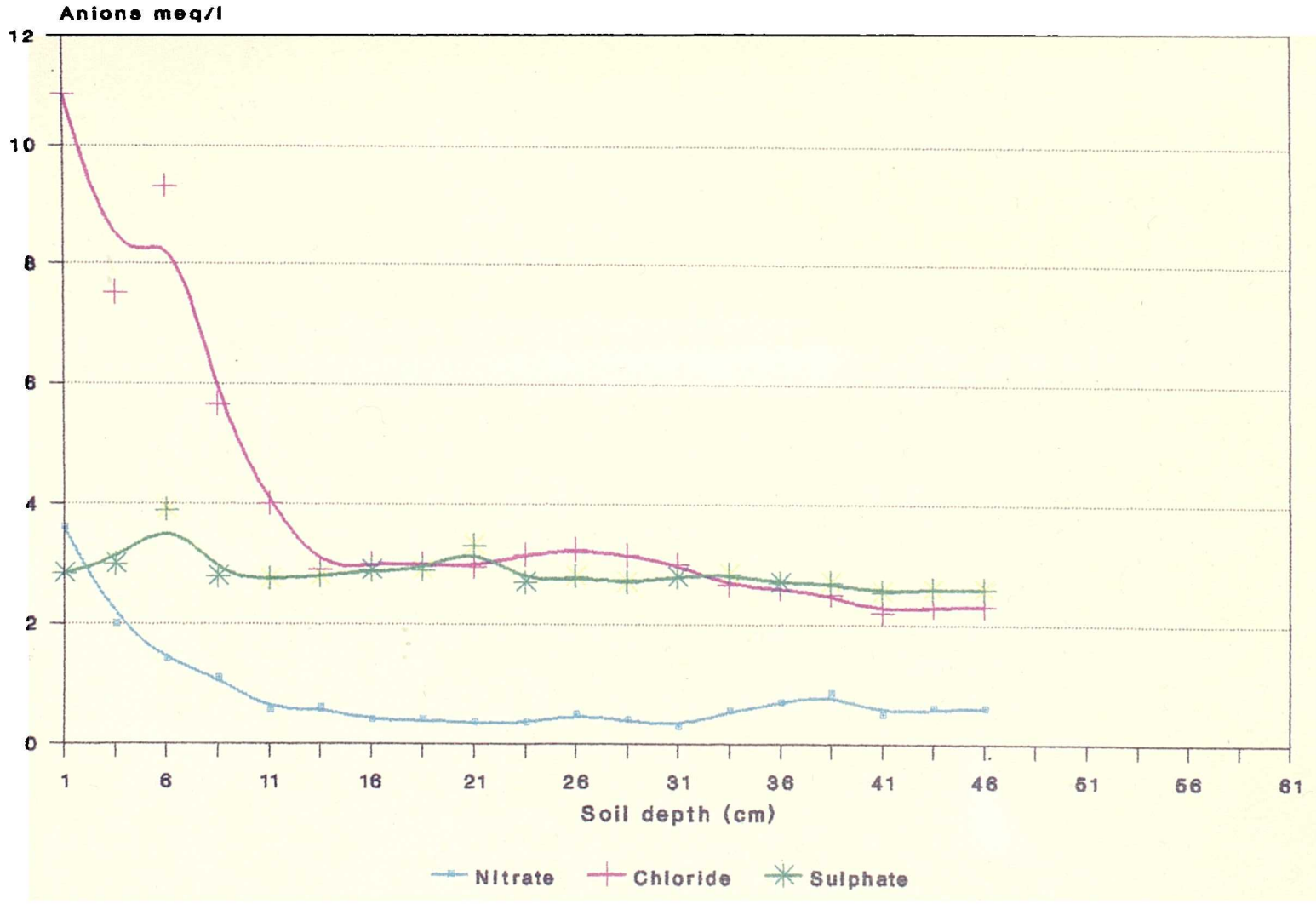


**Fig.4.4.12a Principal anions: chloride, nitrate and sulphate in Haw Wood soil profile 1987 (extracted soil water)**

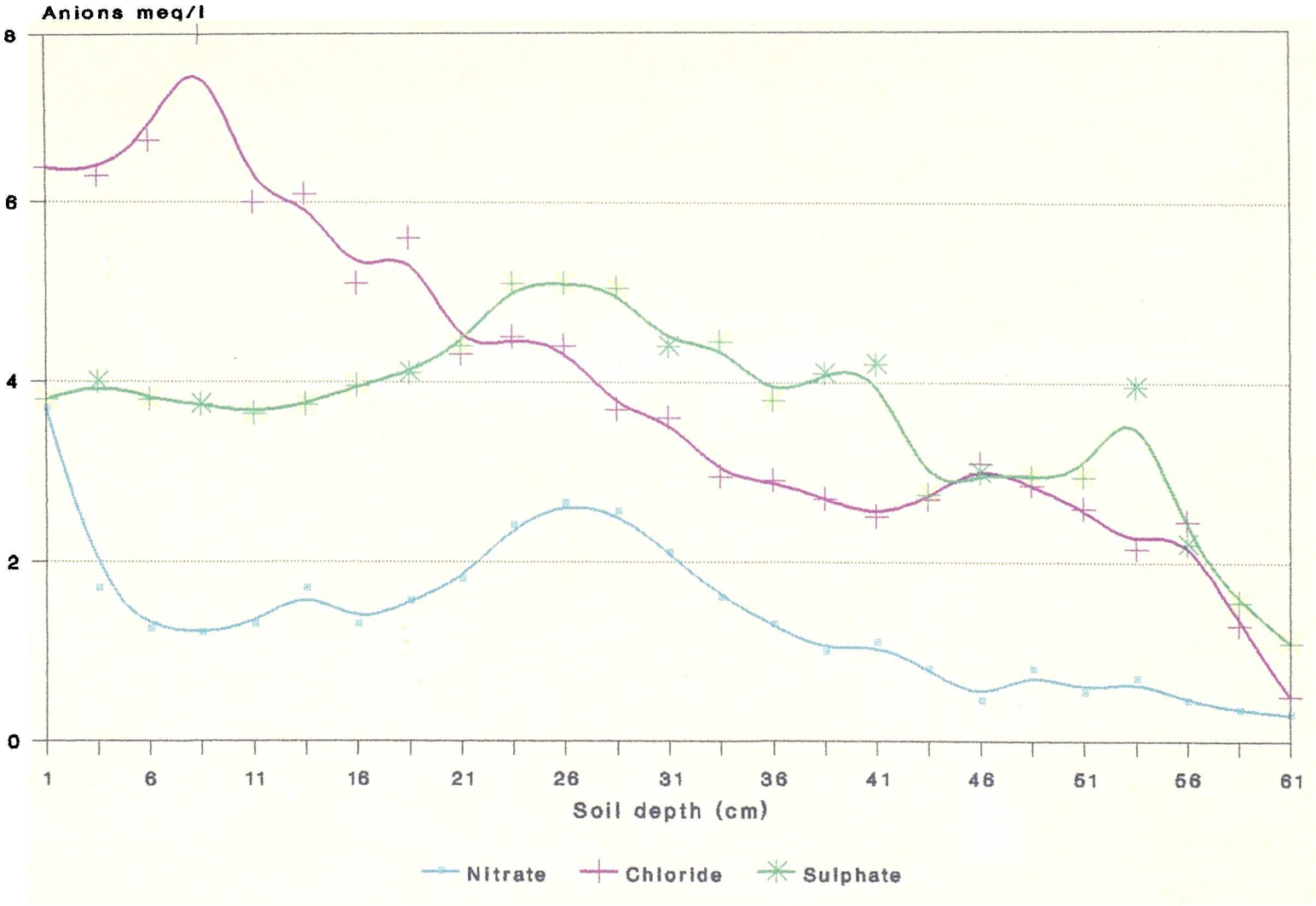


**Fig.4.4.12b Principal anions: chloride, nitrate and sulphate in Hallen Wood soil profile 1987 (extracted soil water)**

**Table 4.4.5 Correlation Coefficients Between Soluble Anions and Cations in Solution From 1-46cm Depth in Haw Wood**

| Soluble Anions | Soluble Cations | | | | | | |
|---|---|---|---|---|---|---|---|
| | Na | K | Mg | Ca | Al | Fe | Mn |
| $Cl^-$ | 0.567 | 0.779* | 0.750* | 0.787* | 0.316 | -0.261 | 0.625 |
| $NO_3^-$ | 0.451 | 0.757* | 0.603 | 0.684 | 0.186 | 0.130 | 0.450 |
| $SO_4^{2-}$ | 0.768* | 0.790* | 0.760* | 0.784* | 0.600 | -0.216 | 0.779* |

n = 17 * : p < 0.1%

---

**Table 4.4.6 Correlation Coefficients Between Soluble Anions and Cations in Solution From 1-61cm Depth in Hallen Wood**

| Soluble Anions | Soluble Cations | | | | | | |
|---|---|---|---|---|---|---|---|
| | Na | K | Mg | Ca | Al | Fe | Mn |
| $Cl^-$ | 0.901* | 0.781* | 0.189 | 0.532 | 0.877* | 0.775* | 0.868* |
| $NO_3^-$ | 0.517 | 0.788* | 0.325 | 0.714* | 0.284 | 0.432 | 0.525 |
| $SO_4^{2-}$ | 0.540 | 0.711* | 0.538 | 0.767* | 0.260 | 0.395 | 0.488 |

n = 24 * : p < 0.1%

---

**Table 4.4.7 Correlation Coefficients Between Soluble Anions and Heavy Metals in Solution From 1-51cm Depth in Hallen Wood**

| Soluble Anions | Soluble Heavy Metals | | | |
|---|---|---|---|---|
| | Cd | Cu | Pb | Zn |
| $Cl^-$ | 0.786** | 0.802** | 0.733** | 0.717** |
| $NO_3^-$ | 0.561* | 0.188 | 0.577* | 0.675* |
| $SO_4^{2-}$ | 0.460 | 0.073 | 0.502 | 0.580* |

n = 20 * : p < 1% ** : p < 0.1%

**Table 4.4.8 Correlation Coefficients of Solution Sulphate and Calcium with Soil Environmental Factors in Hallen Wood Soil**

| | Depth | pH | % Carbon | Bulk Density | Exchangeable Bases | Exchangeable Acidity | CEC | % Base Saturation |
|---|---|---|---|---|---|---|---|---|
| $SO_4^{2-}$ | -0.589 | 0.737* | 0.637 | -0.665* | -0.581 | 0.676* | 0.661* | -0.722* |
| $Ca^{2+}$ | 0.549 | -0.671* | 0.551 | -0.585 | -0.545 | 0.619 | 0.592 | -0.647* |

n = 24 * : $p < 0.1\%$

---

**Table 4.4.9 Correlation Coefficients of Soluble Calcium with Other Soluble Metals in Hallen Wood Soil**

| | Mg | K | Na | Al | Fe | Mn | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 0.789* | 0.770* | 0.615 | 0.300 | 0.380 | 0.630 | 0.522 | 0.262 | 0.160 | 0.444 |

$n \approx 24$ (n = 20 for Cd, Cu, Pb and Zn) * : $p<0.1\%$

mobile/easily leached element in the soil solution, then a tentative suggestion may be offered that leachability is expressed in the correlation coefficient that an element has with calcium. This would suppose that the order of leaching was as follows:

| | | |
|---|---|---|
| Major Cations | : | Ca, Mg > K > Na |
| Minor and Trace Cations | : | Mn > Cd > Zn > Fe > Al > Cu > Pb |
| Anions (Table 4.6) | : | $SO_4^{2-} > NO_3^- > Cl^-$ |

The sequence demonstrated by the anions is interesting in that the chloride ion is usually considered to be the most mobile of the three anions. In fact a reverse order in the sequence would normally be considered more appropriate as $Cl^-$ and $NO_3^-$ are not involved in specific adsorption whereas $SO_4^{2-}$ is (Johnson and Cole 1980). The retention of anions in soils therefore usually follows the order (Wiklander 1980):

$$H_2PO_4^- > SO_4^{2-} > NO_3^- \approx Cl^-$$

However, the close association that chloride had with soluble minor and trace elements (see Table 4.4.6 and Table 4.4.7) suggests that in the Hallen soil system chloride was not being leached to the degree that sulphate was being leached. It is often assumed that $Cl^-$ input is accompanied by an equivalent amount of $Na^+$ or other sea-salt cations, but this is not necessarily the case (Skeffington 1983). However, in the acidified system of Hallen Wood, the correlation between $Na^+$ and $Cl^-$ is very strong, $r = 0.901$ (see Fig.4.4.13); perhaps a result of the fact that the site lies only a few kilometres downwind of the Bristol Channel. Therefore if it is assumed that the $Cl^-$ input is primarily as a salt, then chloride mobility should have little net effect on net cation removal from forest ecosystems (Johnson and Cole 1980). The equivalent distribution of $Na^+$ and $Cl^-$ was also similar in Haw Wood except that $Na^+$ levels were a little more depressed in the top 8.5cm which was possibly due to the higher % carbon contents of Haw topsoil at 3.5% or greater. This might help to explain the lower correlation coefficient between $Na^+$ and $Cl^-$ in the Haw profile ($r = +0.567$).

It is interesting that in Fig.4.4.13 $Na^+$ became more abundant than chloride at depths 26-61cm in Hallen wood, and 13.5-23.5cm and 38.5-46cm in Haw Wood. This coincides with the depths at which the $SO_4^{2-}$ anion was co-dominant or dominant with the chloride ion in both soils (see Fig.4.4.12). This

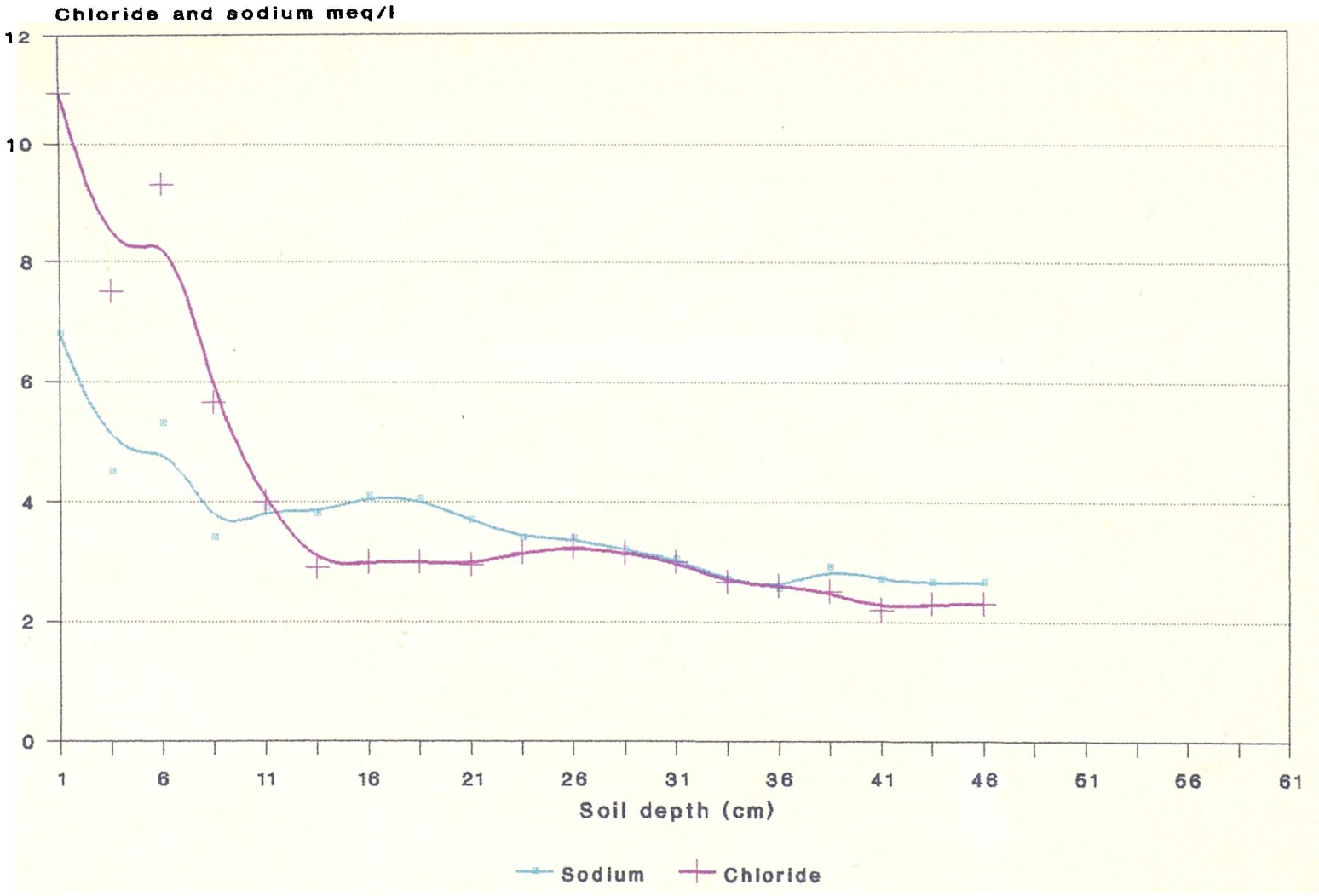


**Fig.4.4.13a Chloride and Sodium in water extractions from 1987 Haw Wood soil profile**

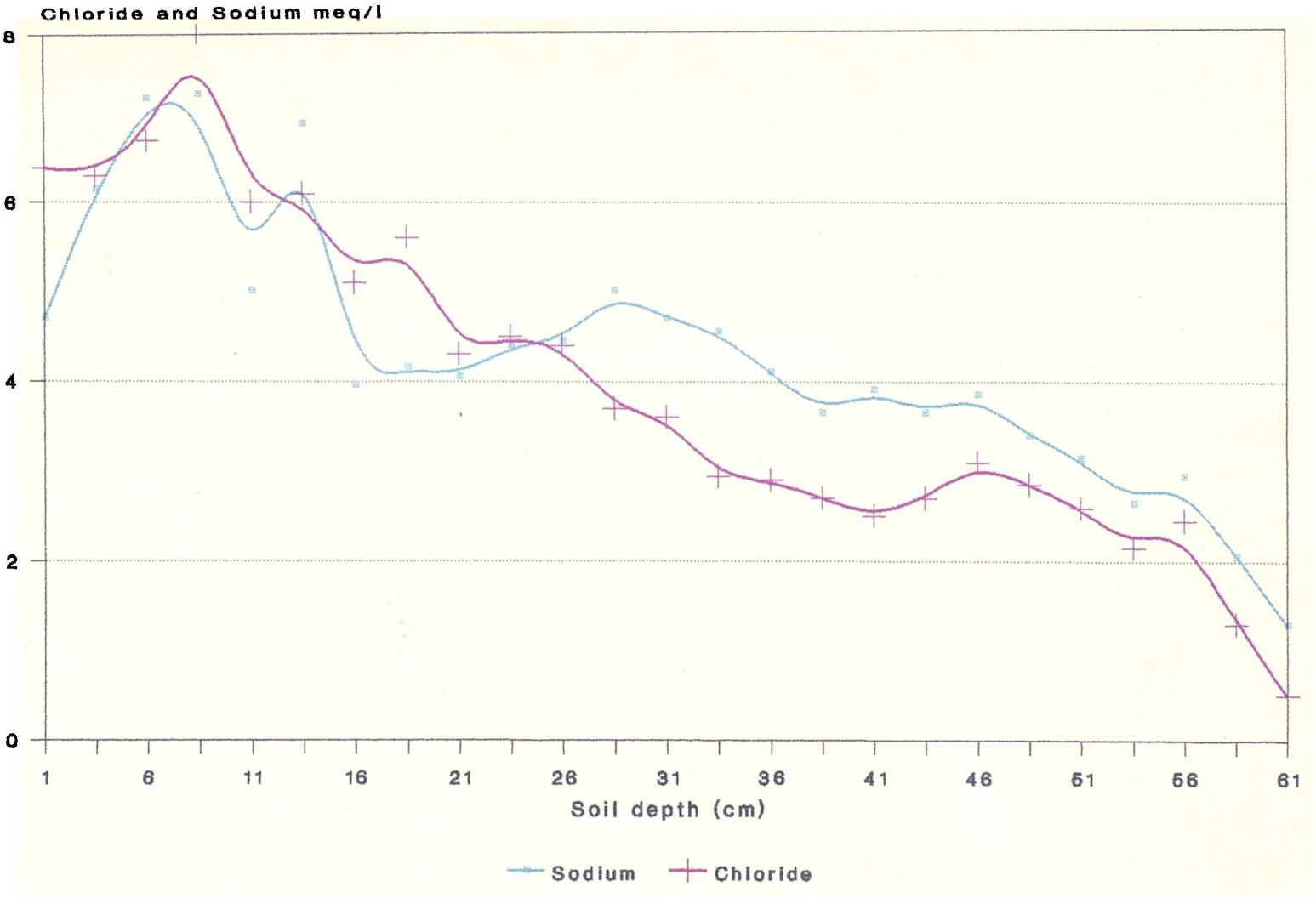


**Fig.4.4.13b Chloride and Sodium in water extracts from 1987 Hallen Wood soil profile**

increased displacement of $Na^+$ may therefore be a response to acidification of the soil at depth related to the higher sulphate levels in solution. The anion needed for leaching of cation bases appears in the soil solution as a proton acid and can thus drive the acidification (Ulrich and Matzner 1987). If sulphate saturation is reached in a soil then leaching of both sulphate and associated base cations can occur (Billet *et al.*1990, Cresser *et al.*1988, Dahigren *et al.*1990, Galloway *et al.*1983). The fact that the soluble anion levels in the Hallen soil at depth were dominated by sulphate ions, which themselves were associated with the leaching of calcium (and magnesium) might suggest that sulphate loading within the soil had occurred. The sulphuric acid plant located adjacent to the Avonmouth smelter is associated with sulphurous gas emissions.

In a study by Van Breeman and Jordens (1983) of woodlands affected by atmospheric ammonium sulphate inputs, marked covariation between the concentration of nitrate, calcium and aluminium was found in the soil solution, indicating that nitric acid had mobilised calcium and aluminium from solid phases. In most cases sulphate concentrations were poorly correlated with concentrations of calcium and aluminium which indicated that for leaching of cations, sulphuric acid was less important than nitric acid. One of the reasons put forward for the difference in behaviour between the two anions was that sulphate was more strongly adsorbed to the soil. With respect to the soluble sulphate in the Hallen soil, the anion was found to be in association with the leaching of calcium in a profile that would appear to be becoming more acidified with time. This would support the idea that the high sulphate input into the Hallen soil system might be a factor that should be considered.

Morrison (1983) and Morrison and Foster (1987) suggested a three stage process of element loss in soils subjected to dilute sulphuric acid input:

(a) Soils exhibit considerable initial resistance, with sulphate movement hampered by strong sulphate adsorption.
(b) Sulphate adsorption capacity is saturated and bases move freely with sulphate ions.
(c) Prolonged exposure to acid solutions may result in increased weathering of silicate minerals of sufficient magnitude to compensate eventually for losses associated with the stripping of exchangeable reserves, so that:

    (1) Bases are depleted.
    (2) $H^+$ ions increasingly dominate charge composition.
    (3) Substantial mobilisation of trace metals occurs.

These three stages somewhat reflect the processes at work in the bottom (stage a), middle (stage b) and top (stage c) of the Hallen soil profile. Hence the possibility of acid deposition / precipitation into the Hallen Wood system should not be ruled out. The fact that nitrous and sulphurous gases are emitted by the sulphuric acid plant, ICI chemicals and Norsk Hydro Fertilizers at Avonmouth, and considering that the pH of precipitation can attain a very high acidic reaction (< pH3.5 - Manning 1978) at Avonmouth, all suggest that acid deposition is a probable phenomenon in the area.

The correlation data for calcium in Haw Wood are given in Table 4.4.10. If again, calcium is taken to be the most easily leached element in the soil the order of most easily leached elements was:

| | | |
|---|---|---|
| Major Cations | : | Ca, Mg > K > Na |
| Minor and Trace Cations | : | Mn > Zn, Cu, Cd > Al > Fe |
| Anions (Table 4.5) | : | $Cl^- > SO_4^{2-} > NO_3^-$ |

The sequence of leachability is not as clear as in Hallen Wood as most of the elements / compounds were highly related to organic matter (% carbon). The trace metals have been grouped together as Cd and Cu were measured on FAAS and hence many values measured were close to the detection limit. Pb is not included as most values were at or below the detection limit of FAAS. Chloride would appear to be the most mobile anion in the soil in relation to calcium solubility. However sulphate correlates well with Na, K, Ca and especially with Mg which indicates that the anion is probably an important counterion with respect to the solubility of these four metals (see Table 4.4.5).

The soluble nitrate distributions in both woodland soils is also of great interest. In Hallen Wood at about mid-profile depth, there was up to 5 times as much soluble nitrate as in Haw Wood (see Fig.4.4.12). Fig.4.4.12 also illustrates that the soluble nitrate in the Hallen profile was in a wave distribution not dissimilar to the Cd and Zn distributions (easily exchangeable, total extractable and total metal concentrations). The same was also true of the distributions of nitrate, Cd and Zn in Haw Wood (see Table 4.4.11). The variables that are in bold type (exchangeable Cd, Zn and K) are strongly associated with soluble $NO_3^-$ in both soils. It has been suggested in Chapter 3 Section 6 that in these woodland soils K was more specifically adsorbed to the clay in these woodlands than the other Group IA and IIA metals (Na, Mg, Ca), and hence the distribution of exchangeable K was allied to those of Cd and Zn

**Table 4.4.10 Correlation Coefficients of Soluble Calcium with Other Soluble Metals in Haw Wood**

| | Mg | K | Na | Al | Fe | Mn | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 0.971 | 0.951 | 0.918 | 0.680 | -0.286 | 0.916 | 0.718 | 0.840 | N.A. | 0.894 |

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**Table 4.4.11 Correlation Coefficients of Soluble Nitrate with Exchangeable Metals in Haw Wood and Hallen Wood Soils**

| $NO_3^-$ | Na | K | Mg | Ca | Al | Fe | Mn | Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Haw | -0.251 | **0.730*** | 0.302 | -0.185 | -0.026 | 0.164 | 0.282 | **0.908*** | 0.534 | 0.198 | **0.925*** |
| Hallen | -0.752* | **0.815*** | -0.662* | -0.571 | 0.684* | 0.258 | 0.799* | **0.884*** | 0.892* | 0.170 | **0.904*** |

n = 17 (Haw) n = 24 (Hallen) n = 20 (Hallen heavy metals)
* : $p < 0.1\%$

(and therefore correlates well with soluble $NO_3^-$). The fact that soluble $NO_3^-$ is so highly correlated with Cd and especially Zn appears to be something of an anomaly. However, if all the soluble anions and cations are correlated with exchangeable metals (0.1M $NH_4NO_3^-$ extractable) in both woodland soils then a distinct pattern of behaviour is illustrated (see Tables 4.4.12 and 4.4.13).

In Haw Wood (Table 4.4.12) the soluble metals and anions fell into two distinct groups:

(a) Aluminium and iron that are principally correlated with their own exchangeable metal distributions.
(b) The rest which are principally correlated with exchangeable Cd, Zn, Cu and exchangeable K.

In Hallen Wood (Table 4.4.13) there were three groups of solutes:

(a) Anions and metals associated with the dissolution / exchangeability of iron and aluminium, and whose solubility decreases as the exchangeable calcium and magnesium increases.
(b) Soluble magnesium, calcium, nitrate and sulphate which are associated with exchangeable Cd, Zn, Cu and exchangeable K (c.f. (b) for Haw Wood).
(c) Soluble K which is affiliated to both groups (a) and (b).

The results for Haw Wood illustrate how soluble forms of anions and metals are related mainly to the distribution of organic matter in the soil as the distributions of exchangeable Cd, Zn, Cu and K correlate highly with % carbon (more than any other environmental variable). In Hallen Wood the majority of solutes are related to the exchangeable hydrogen distribution with depth, with which exchangeable magnesium, calcium and aluminium are highly correlated. Otherwise the solutes calcium, magnesium, nitrate and sulphate are associated with exchangeable Cd, Cu, Zn and K (and indeed Mn) which are principally correlated to pH and % base saturation more than any other soil environmental variable. Soluble K was unique in its association between the two solute groups, possibly as a result of its affinity for the 2:1 layer clay minerals in the Hallen and Haw soils. Interestingly, group (a) and group (b) solutes for Hallen soil fall into two groups:

**Table 4.4.12 Correlation Coefficients of Soluble Anions and Metals with Exchangeable Metals in Haw Wood**

| Soluble Anions & Metals | Exchangeable Metals | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Na | K | Mg | Ca | Al | Fe | Mn | Cd | Zn | Cu | Pb |
| Na | | 0.829 | 0.770 | | 0.701 | | 0.800 | | | 0.837 | |
| K | | 0.924 | | | | | | 0.854 | 0.898 | 0.843 | |
| Mg | | 0.912 | 0.753 | | | | 0.787 | 0.738 | 0.783 | 0.857 | 0.727 |
| Ca | | 0.910 | 0.706 | | | | 0.750 | 0.793 | 0.844 | 0.815 | |
| Al | | | | | 0.924 | | | | | | |
| Fe | | | -0.761 | | | 0.997 | -0.729 | | | | |
| Mn | | 0.833 | 0.721 | | | | 0.765 | | | 0.780 | 0.705 |
| Cd | | 0.838 | | | | | | 0.895 | 0.876 | 0.795 | |
| Zn | | 0.914 | | | | | | 0.960 | 0.984 | 0.778 | |
| Cu | | 0.812 | 0.751 | | | | 0.768 | | | 0.922 | 0.707 |
| Pb | | 0.913 | | | | | | 0.942 | 0.965 | 0.751 | |
| $Cl^-$ | | 0.846 | | | | | | | 0.765 | | |
| $NO_3^-$ | | 0.730 | | | | | | 0.908 | 0.925 | | |
| $*SO_4^{2-}$ | | 0.646 | | | | | 0.524 | | 0.530 | 0.643 | |

Correlations of ±0.700 or greater are shown

* : $SO_4^{2-}$ has no correlations greater than ±0.700
so the highest correlations are shown

**Table 4.4.13 Correlation Coefficients of Soluble Anions and Metals with Exchangeable Metals in Hallen Wood**

| Soluble Anions & Metals | Exchangeable Metals | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Na | K | Mg | Ca | Al | Fe | Mn | Cd | Zn | Cu | Pb |
| Na | | | -0.835 | -0.825 | 0.734 | 0.773 | 0.746 | | | | |
| K | -0.944 | 0.855 | -0.896 | -0.850 | 0.919 | | 0.923 | 0.852 | 0.921 | 0.899 | |
| *Mg | | 0.440 | | | | | 0.391 | 0.366 | | 0.487 | |
| Ca | | 0.737 | | | | | 0.704 | 0.732 | 0.703 | 0.820 | |
| Al | | | -0.821 | -0.849 | 0.780 | 0.969 | | | | | 0.803 |
| Fe | -0.840 | | -0.846 | -0.850 | 0.884 | 0.801 | | | | | |
| Mn | -0.770 | | -0.863 | -0.862 | 0.840 | 0.928 | 0.842 | | | | |
| Cd | -0.737 | | -0.872 | -0.854 | 0.829 | 0.751 | 0.760 | | | | |
| Zn | -0.742 | | -0.850 | -0.788 | 0.829 | | 0.731 | | 0.741 | 0.759 | |
| Cu | | | -0.717 | -0.737 | | 0.839 | | | | | 0.804 |
| Pb | -0.796 | | -0.862 | -0.808 | 0.861 | | 0.839 | | | | |
| $Cl^-$ | -0.802 | | -0.918 | -0.925 | 0.874 | 0.877 | 0.763 | | | | |
| $NO_3^-$ | -0.752 | 0.815 | | | | | 0.799 | 0.884 | 0.904 | 0.892 | |
| $SO_4^{2-}$ | | 0.831 | | | | | 0.788 | 0.849 | 0.789 | 0.883 | |

Correlations of ±0.700 or greater are shown

* : Mg has no correlations greater than ±0.700
so the highest correlations are shown

(i) Na, $Cl^-$, Al, Fe, Mn, Cd, Zn, Cu, Pb - these elements are all classified as micro-nutrients or non-essential nutrients.

(ii) Ca, Mg, $NO_3^-$, $SO_4^{2-}$ - these are all macronutrients (K is also a macronutrient).

Thus, depending on the relative production and movement of solute down the soil profile, the distribution of a solute such as $NO_3^-$ which is highly correlated with exchangeable Cd and Zn in both soils might have been dependent on biological / plant root activity within the soil. The 2.5% acetic acid (HOAc) extractable levels of Cd in particular, within the Hallen Profile and at the top of the Haw profile were exceptionally high. In Hallen Wood, between 21-33.5cm there was between 4.3-4.5μg/g HOAc extractable cadmium and up to nearly 135μg/g HOAc extractable zinc. These values are (depending on the bulk density of the soils) in the upper limit of a survey carried out on soils of England and Wales by Archer and Hodgson (1987). Their highest data for 2.5% HOAc extractable Cd and Zn were 4.3μg/$cm^3$ and 138μg/$cm^3$ of soil respectively. Archer and Hodgson's upper limit of their normal extractable ranges are 1.9μg/$cm^3$ for Cd and 28μg/$cm^3$ for Zn.

Solute peaks such as those of nitrate in Hallen Wood might have been purely the result of the effect of toxic levels of metals such as Cd and Zn on biological / plant root activity in the soil. For example, Cd levels might have been sufficiently toxic at HOAc extractable levels greater than 4μg/g which would coincide with the nitrate peak at 21-33.5cm depth in the Hallen profile (see Fig.4.4.12). Correlation coefficients for solutes with 2.5% HOAc extractable Cd and Zn are shown in Table 4.4.14. It is plausible that levels of available Cd and Zn in Hallen Wood and the topsoil of Haw Wood were high enough to disrupt the uptake of the "primary" or "fertiliser" elements in both woodlands to some degree. Therefore, this would encourage "Primary" macronutrients such as nitrogen ($NO_3^-$) and potassium to correlate very highly with extractable Cd and Zn in both soils. It would also help to explain how the build up of exchangeable potassium has occurred in the mid-profile of Hallen Wood (due to the lack of biological/plant root activity and specific adsorption of K to forms of 2:1 clay minerals), and why exchangeable K correlates so well with exchangeable Cd and Zn within both woodlands (see Chapter 3 Section 6). Furthermore, it would also help explain the presence of the other primary element, phosphorus, which was detected within Hallen Wood. The "secondary" macronutrient element, calcium, also significantly correlates with both extractable Cd and Zn in both soils. The other "secondary" elements,

**Table 4.4.14 Correlation Coefficients of Soluble Anions and Metals with 2.5% HOAc Extractable Cd and Zn**

Hallen Soluble

| 2.5% HOAc | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Al^{3+}$ | $Fe^{2+}$ | $Mn^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 0.474 | 0.777* | 0.414 | 0.745* | 0.179 | 0.422 | 0.431 | 0.316 | 0.499 | -0.185 |
| Zn | 0.545 | 0.902* | 0.299 | 0.733* | 0.375 | 0.610 | 0.605 | 0.599 | 0.735* | 0.144 |

| 2.5% HOAc | $Pb^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|
| Cd | 0.393 | 0.412 | 0.871* | 0.859* |
| Zn | 0.642 | 0.562* | 0.930* | 0.809* |

n = 24 n = 20 for Cd, Zn, Cu, Pb * : $p < 0.1\%$

Haw Soluble

| 2.5% HOAc | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Al^{3+}$ | $Fe^{2+}$ | $Mn^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 0.671 | 0.871* | 0.758* | 0.814* | 0.353 | -0.130 | 0.650 | 0.881* | 0.970* | 0.619 |
| Zn | 0.696 | 0.905* | 0.797* | 0.857* | 0.378 | -0.107 | 0.686 | 0.870* | 0.985* | 0.639 |

| 2.5% HOAc | $Pb^{2+}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|
| Cd | 0.957* | 0.749* | 0.920* | 0.489 |
| Zn | 0.972* | 0.790* | 0.924* | 0.542 |

n = 17 * : $p < 0.1\%$

## Table 4.4.16 Anions in Haw and Hallen Wood Profile Soils

| Location | Depth cm | pH ($H_2O$) | meq/litre $Cl^-$ | meq/litre $NO_3^-$ | meq/litre $SO_4^{2-}$ | mg/l $SO_4$:Cl Ratio |
|---|---|---|---|---|---|---|
| Hallen Wood | 0-1 | 4.36 | 6.430 | 3.738 | 3.780 | 3.18 |
| | 1-3.5 | 4.55 | 6.278 | 1.703 | 3.982 | 3.43 |
| | 3.5-6 | 4.37 | 6.684 | 1.271 | 3.810 | 3.08 |
| | 6-8.5 | 4.55 | 8.010 | 1.193 | 3.744 | 2.53 |
| Haw Wood | 0-1 | 5.20 | 10.920 | 3.629 | 2.846 | 1.41 |
| | 1-3.5 | 5.30 | 7.457 | 2.038 | 2.977 | 2.16 |
| | 3.5-6 | 5.65 | 9.296 | 1.380 | 3.934 | 2.29 |
| | 6-8.5 | 5.85 | 5.669 | 1.103 | 2.792 | 2.66 |

---

sulphur and magnesium are only significantly correlated to extractable Cd and Zn in Hallen Wood and Haw Wood respectively.

## 4.4.7. Soluble Inorganic Anions in Fresh Soil Sample Material

Soil: water extractions of ratio 1:2.5 were carried out on fresh soil material. The soil material was collected from Avon, Somerset and Shropshire. Avon sites were at Hallen Wood (ST 554 802), Wetmoor Wood (ST 750 883) and Burrington Coombe (ST 486 584); the Somerset site was at Black Down (ST 485 575); Shropshire sites were at Wenlock Edge (SO 602 997), Benthall Edge (SJ 664 034), The Wrekin (SJ 618 072) and The Ercall (SJ 645 095). The results are shown in Table 4.4.15. The figures for the air dried soils are shown in Table 4.4.16. The soils in Table 4.4.15 and Table 4.4.16 fall into three groups. First, the Haw and Hallen sites which lie in close proximity to the Avonmouth industrial complex. Second, the Shropshire soils that lie in the vicinity of the Ironbridge coal-burning power station. Third, the Somerset and other Avon soils that should not receive highly acidic aerial inputs from industrial complexes.

Making firm conclusions from the data is difficult because one is dealing with an individualistic soil entity for each location. However, it is worth making a few remarks about the data and drawing one important conclusion from it:

## Table 4.4.15 Anions in Avon, Somerset and Shropshire Soil Solutions

| Location | Depth cm | pH ($H_2O$) | meq/litre $Cl^-$ | meq/litre $NO_3^-$ | meq/litre $SO_4^{2-}$ | mg/l $SO_4$:Cl Ratio |
|---|---|---|---|---|---|---|
| Hallen Wood* | 0-1 | 3.55 | 7.211 | 4.645 | 3.958 | 2.96 |
| | 1-3.5 | 3.65 | 6.648 | 4.000 | 5.188 | 4.22 |
| | 3.5-6 | 3.80 | 7.437 | 3.871 | 7.604 | 5.53 |
| | 6-8.5 | 3.95 | 7.944 | 3.742 | 9.000 | 6.13 |
| Wetmoor Wood* | 0-1 | 6.45 | 6.704 | 0.484 | 1.948 | 1.57 |
| | 1-3.5 | 6.30 | 3.761 | 0.387 | 1.542 | 2.22 |
| | 3.5-6 | 6.25 | 2.577 | 0.744 | 1.083 | 2.27 |
| | 6-8.5 | 6.25 | 2.127 | 0.581 | 0.688 | 1.75 |
| Black Down | 0-5 | 3.40 | 2.141 | 0.323 | 1.313 | 3.32 |
| (Mendip peat A) | 5-10 | 3.55 | 1.859 | 0.290 | 0.823 | 2.39 |
| Black Down | 0-5 | 3.55 | 2.479 | 0.452 | 1.208 | 2.64 |
| (Mendip peat B) | 5-10 | 3.70 | 1.690 | 0.097 | 0.385 | 1.23 |
| Burrington Coombe | 0-5 | 5.90 | 3.718 | 0.774 | 1.177 | 1.71 |
| (grassland) | 5-10 | 6.30 | 2.535 | 0.613 | 1.052 | 2.24 |
| Wenlock Edge* | 0-5 | 5.35 | 4.158 | 1.171 | 2.193 | 2.85 |
| (woodland) | 5-10 | 5.44 | 3.718 | 1.816 | 1.897 | 2.76 |
| Benthall Edge | 0-5 | 4.90 | 3.527 | 1.561 | 1.956 | 3.00 |
| (woodland A) | 5-10 | 4.79 | 3.561 | 2.652 | 2.164 | 3.29 |
| Benthall Edge | 0-5 | 3.75 | 3.329 | 6.981 | 2.939 | 4.77 |
| (woodland B) | 5-10 | 3.84 | 2.958 | 4.100 | 2.532 | 4.63 |
| Wrekin | 0-5 | 3.72 | 4.868 | 5.900 | 2.963 | 3.29 |
| (woodland) | 5-10 | 3.80 | 4.563 | 3.913 | 3.028 | 3.59 |
| Ercall Woods | 0-5 | ‡ | 5.504 | 1.097 | 2.978 | 2.93 |
| (*Deschampsia flexuosa* A) | 5-10 | | 5.679 | 1.203 | 2.807 | 2.67 |
| Ercall Woods | 0-5 | ‡ | 6.794 | 0.897 | 2.827 | 2.25 |
| (*Vaccinium myrtillus* B) | 5-10 | | 4.873 | 0.597 | 2.060 | 2.29 |
| Ercall Woods | 0-5 | ‡ | 3.386 | 5.694 | 1.826 | 2.92 |
| (Hyacinthoides *non-scripta* A) | 5-10 | | | | | |

‡ : pH3.50-4.00
* : heavy clay soils

(a) Some of the highest chloride levels were found in the Hallen and Haw Wood soils - these two locations being closest to saline waters (the Severn Estuary).
(b) Chloride was always the dominant topsoil anion in relation to the sulphate ion except in the fresh soil of Hallen Wood.
(c) Nitrate was generally the least abundant anion except in three of the Shropshire soils. High values of nitrate are also found in the fresh Hallen soil.
(d) The highest water soluble sulphate levels were clearly found in the Hallen soil.

The largest $SO_4$: Cl ratios were in the fresh Hallen soil and the Benthall Edge "B" soil (see Table 4.4.15). These two soils were located closest to sulphurous gas emitters. The Benthall Edge soil was located within an area that was in close proximity with a coal burning power station and a site of previous industrial activity (in the 18th/19th century e.g. an iron foundry). The Hallen soil was collected close to a sulphuric acid plant which is part of the smelting works at Avonmouth. A comparison of the ratio of $SO_4$: Cl in soil solutions, seepage waters and spring waters allows a quantitative estimate of the relative enrichment in sulphate due to acid deposition (Ulrich 1986). In Germany the ratio of $SO_4$ (mg/l): Cl (mg/l) in sea spray was 0.05, in wet deposition 0.5-1.4 and in forested areas up to 2.2 (due to dry deposition); and in soil solutions of highly variable sites between the coast and the Alps, the ratio was between 0.5 and 5 (Ulrich 1986). The high ratio values found in the fresh Hallen topsoil would suggest that periodic episodes of acid deposition / precipitation into the Hallen soil system is a factor worth considering, and would be a likely cause of the comparatively rapid acidification of the Hallen profile with time (see Chapter 2 Section 3). Levels of chloride in the fresh Hallen soil and air dried soil were quite similar (see Table 4.4.15, Table 4.4.16), but levels of nitrate and sulphate in the fresh soil were much more elevated, corresponding with a much reduced pH. Hallen Wood is located downwind of a major sulphuric acid plant and close to major nitric acid plants (Martin and Coughtrey 1987). Obviously levels of nitrate in the Hallen soil were no higher than those recorded for some of the Shropshire soils; however they were much higher than those recorded in other heavy clay soils. If Hallen Wood is exposed to acid deposition, then so too should be Haw Wood. However, if the burden of heavy metals in Haw Wood is less than Hallen Wood (see Chapter 2 Section 3), then it is reasonable to suppose that so too should be the degree of

acid deposition. Furthermore, Haw Wood is sheltered by Hallen Hill from nitrous gas emitters such as I.C.I. Chemicals that lie in closer proximity to Hallen Wood.

Firmer conclusive evidence of acid deposition into the Hallen system would probably be attained by long term measurement of wet and dry deposition into the woodland system, and by measuring the sulphur and nitrogen loading within the soils. Nevertheless, the high $SO_4$: Cl ratios in Hallen soil and the presence of acidic gas emitters at Avonmouth help to point the finger at acid deposition being the main influence in driving the process of acidification to depth in the Hallen soil. High sulphate and acid deposition as indicated by the $SO_4$: Cl ratios in the soil solution has the following consequences: it drives base cation leaching, and after loss of exchangeable Ca, drives the dissolution and leaching of Al (Ulrich 1986).

## 4.4.8. The Chemical Composition of Haw Wood and Hallen Wood Soil Solutions

Fig.4.4.14 illustrates the chemical composition of soil solutions in both woodland soils. Levels of anions tended to reflect levels of cations. Cations, though, in the upper sections of the profiles had levels slightly higher than those of anions so that the cation: anion ratios in the mineral soils were 1.18 (±0.17) in Haw Wood and 1.15 (±0.16) in Hallen Wood. The greatest departure from electrical neutrality occurred in the litter (1.71 for Haw Wood and 1.37 for Hallen Wood). The departure from electroneutrality was likely to be due to not taking into account organic or bicarbonate anions (Nowak *et al.*1989).

Bicarbonate and carbonate are important anions in calcareous soil solutions because of the dissolution of carbonates in percolating water (Wiklander 1974). In water systems at pH values close to 6.4, $H_2CO_3$ and $HCO_3^-$ are present at comparable concentrations; but below pH6, essentially all are in the form of $H_2CO_3$, and above pH7, essentially all are in the form of $HCO_3^-$ (Drever 1982). The effect of pH on the dissociation of carbonic acid has been illustrated by Binkley *et al.*(1989). Examples of % dissociation that they gave were:

pH6.6 - 65%
pH5.6 - 16%
pH4.6 - 1.6%

The differences in the levels between anions and cations in the litter (see Fig.4.4.14a-b) were likely to be a result of not taking organic anions into

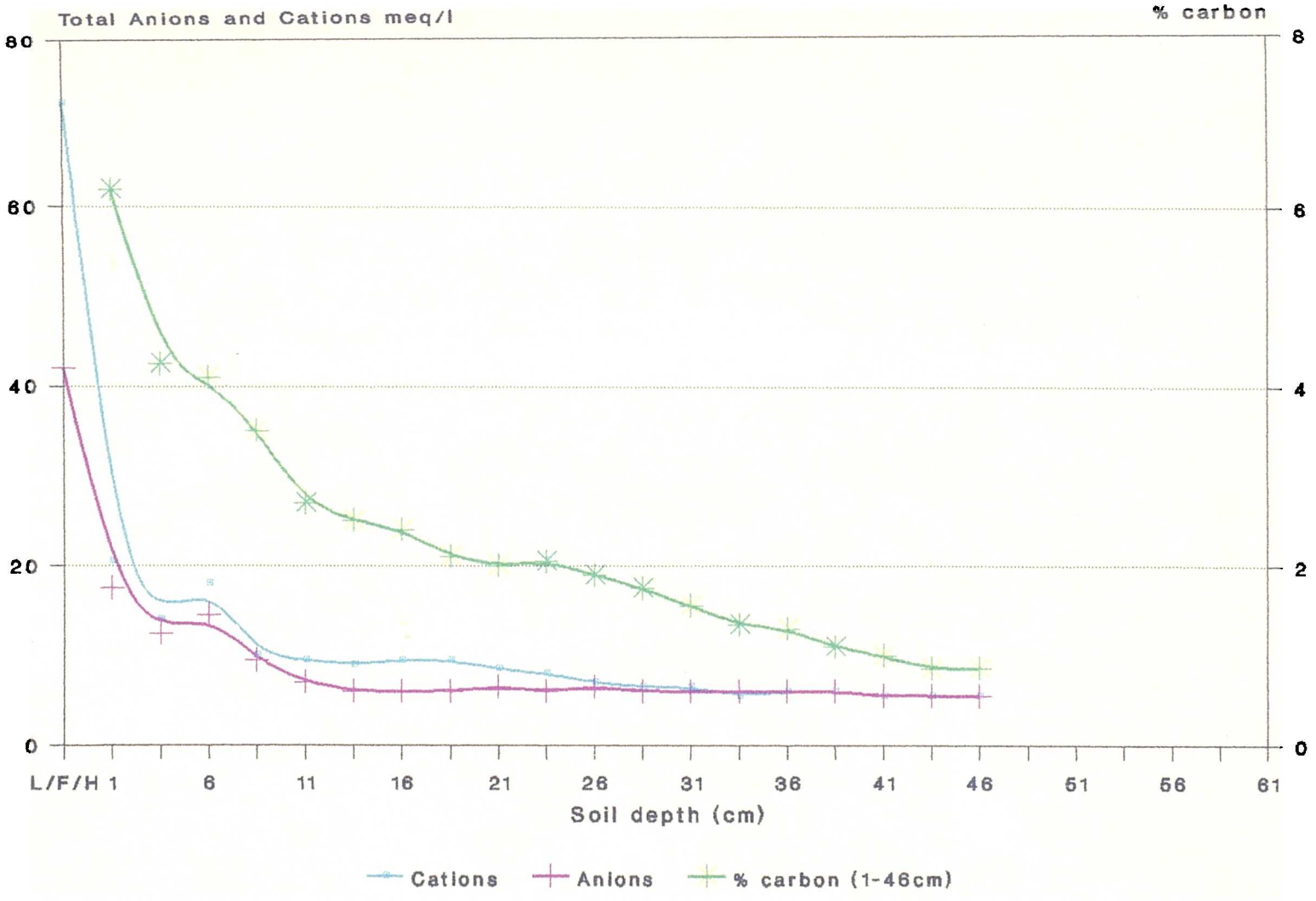


**Fig.4.4.14a Total Anions and Cations in water extracts from Haw Wood (1987) soil profile**

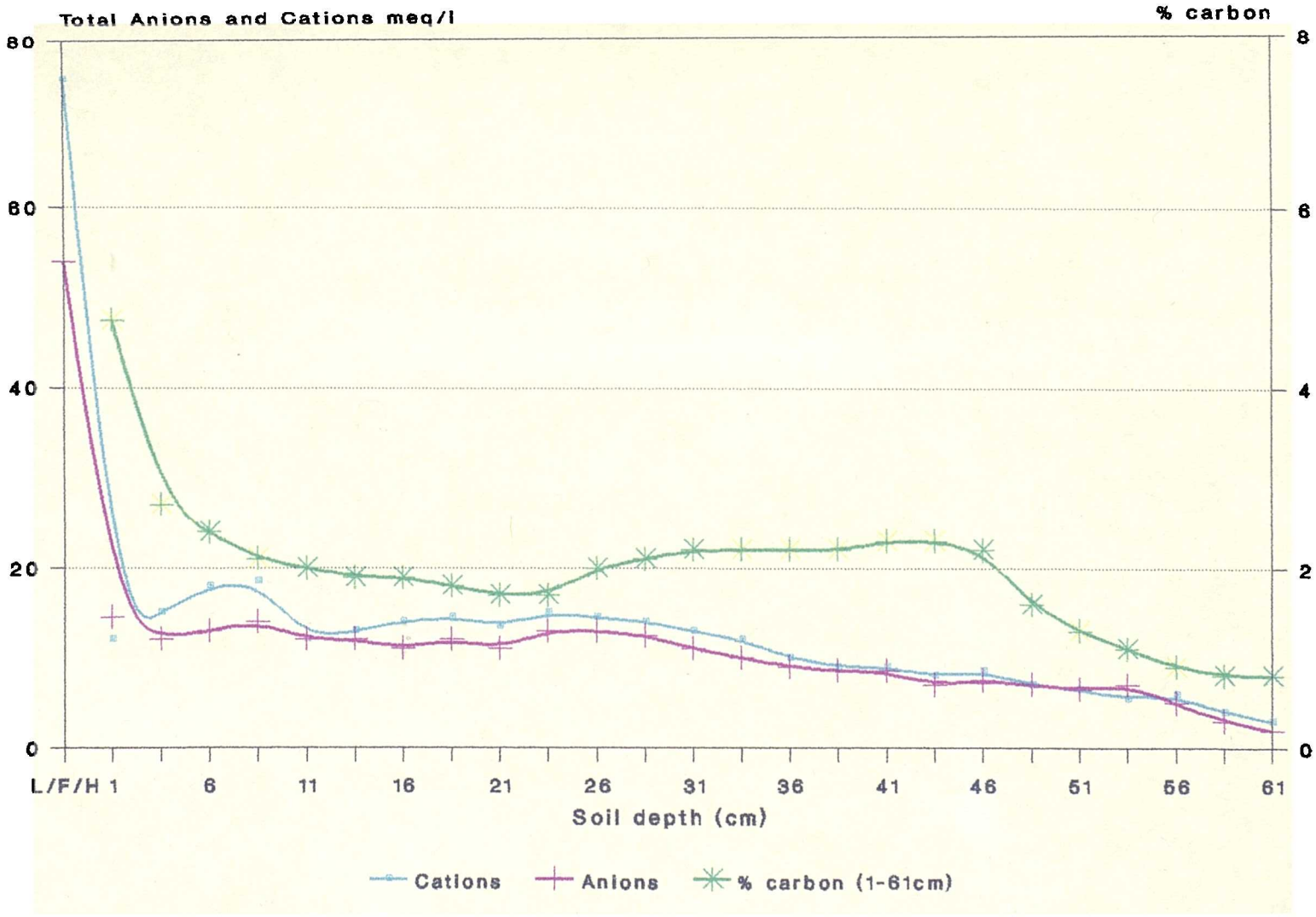


**Fig.4.4.14b Total Anions and Cations in water extracts from Hallen Wood (1987) soil profile**

account. On inspection of Fig.4.4.14a-b it is interesting to note that as the % carbon in the mineral soil falls from circa 2% to below 1.5% (to depth), electrical neutrality was almost attained suggesting that organic anions in the soil solution might have been influential to depths of 46-48.5cm in Hallen Wood and 26-31cm in Haw Wood. Differences between fluxes of cations and of anions are taken as a measure of the flux of organic anions (Matzner and Ulrich 1983). Thus, organic anion equivalent can be determined by charge balance (Bredemeier 1987). In a study by Johnson in 1975, anion-cation balance calculations indicated that organic anions accounted for up to 30-50% of the total anionic component in northern forest ecosystems (Johnson and Cole 1980). If the anion deficit was compensated by organic anions then organic anions would comprise on average within the mineral soil 18.6±9.6% of the negative charge in Haw Wood to 31cm depth (5-34%) and 13.7±7.6% (5-29%) of the negative charge in Hallen Wood to 46cm depth.

Another factor that perhaps should also be considered is that a surplus of storage cations in the soil implies compensatory soil internal $OH^-$ release (alkalinisation) (Bredemeier 1987). The higher pH values recorded in the Hallen 1987 profile indicate the fluctuative variations that a soil can be subjected to; pH values of 0.3-0.5 units higher than previously recorded in the topsoil of Hallen 1984, 1985 profiles might be a result of this effect (see Chapter 2 Section 3).

Anion deficits have been recorded in both "A" and "B" horizons of soils (Freisleben and Rasmussen 1986, Kinniburgh 1986), and the likelihood is that the deficit is as a result of a combination of factors including alkalinisation. However, the anionic input of $HCO_3^-$ from respiratory processes cannot be ruled out, and organic anions are probably accountable for a fair proportion of anion deficit. In an assessment of the soil solution chemistry of Oxfordshire soils, Campbell *et al.*(1989) found that dissolved organic matter was a major constituent in all of the soil solutions including Denchworth Series clay soils and a range of woodland/forest soils.

It is taken as axiomatic that studies of the soil solution *sensu stricto* should be made on fresh, field-moist soils (Campbell *et al.*1989). Chemical changes may occur in stored soils because of drying out, leading to oxidation and an increase in acidity on rewetting (Bartlett and James 1980) and may produce artefacts within the resultant composition of the soil solution (Larsen and Widdowson 1968, Edmeades *et al.*1985). In a study by Haynes and Swift (1989) the effect of rewetting a number of air-dried soil on pH and on accumulation of mineral-nitrogen was examined in a laboratory incubation study

over a period of weeks. The effects of nitrification were least in soils in the lower pH range up to pH5.5. Ammonification occurred in soils over the full range of pH. The increase in microbial growth and activity within a soil on rewetting and incubation is a factor that should be taken into consideration. Periods of solution-soil shaking in excess of a few hours are undesirable because the pH meanders with time and a stable pH is not attained (Conyers and Davey 1988), no doubt, amongst other things, a result of nitrification and/or ammonification. Shaking times should be no longer than 60 minutes as a result (Davey and Conyers 1988). There is also the chance of destabilisation of organic micelles as a consequence of drying soil (Raveh and Avnimelech 1978).

Re-wetting air dry soils and incubating / equilibrating them for 24 hours or more (e.g. Adams *et al.*1980, Elkhalib *et al.*1987, Gillman and Summer 1987, Larsen and Widdowson 1968) provides the opportunity for nitrification / ammonification to take place as well as associated changes in pH. The policy of extracting the soil solution as soon as possible after collecting the soil seems to be the most sensible approach (Campbell *et al.*1989, Ross and Bartlett 1990). Obviously with respect to the Hallen Wood and Haw Wood soils, the sample material has been air dried. The sheer prospect of preparing soil and separating soil solutions from the bulk quantity of profile incremental layers of fresh soil would defy the realms of possibility as regards obtaining soil solution under "optimal" conditions (or at least within a matter of 6 hours e.g. Campbell *et al.* 1989).

There has been one school of thought that has taken on the idea of an equilibrium soil solution (ESS) - a saturation extract after a contact time of 24 hours between water field-fresh soil (ratio water: soil 0.8ml/g) (e.g. Matzner 1983, Skeffington 1983, Ulrich *et al.*1980, Ulrich 1983) based on the work by Ulrich and Khanna (1972). Another group of researchers have used 1:2 soil: water extracts to estimate the chemical compositions of soil solutions (Sonneveld *et al.* 1990) e.g. Gysi (1981). The danger is that in a dilute soil extraction, ionic concentrations can deviate from the "actual" soil solutions (Ulrich 1972, Sonneveld *et al.*1990) although the constituent concentrations in 1:2 extracts have proved to be closely correlated with those in saturation extracts (Sonneveld and Van den Ende 1971). 1:2 extracts have been used in routine soil testing for many years in the Dutch greenhouse industry (Sonneveld *et al.* 1990).

In comparing the solution chemistry within and between Haw Wood and Hallen Wood soils, a 1:2.5 soil: water extract was deemed adequate. The extract was shaken for a maximum period of one hour so that solution

**Table 4.4.17 Comparison of the Composition of Soil Solutions Collected from Denchworth and Related Clay Soil Series**

| Location | Depth (cm) | pH | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | milliequivalents per litre | | | | | | |
| Wetmoor Wood* | 0-1 | 6.45 | 6.704 | 0.484 | 1.948 | - | - | - | - |
| (Denchworth Series) | 1-3.5 | 6.30 | 3.761 | 0.387 | 1.542 | - | - | - | - |
| | 3.5-6 | 6.25 | 2.577 | 0.774 | 1.083 | - | - | - | - |
| | 6-8.5 | 6.25 | 2.127 | 0.581 | 0.688 | - | - | - | - |
| Haw Wood** | 36-38.5 | 6.15 | 2.504 | 0.858 | 2.736 | 2.903 | 0.927 | 0.190 | 1.606 |
| (Denchworth Series) | 38.5-41 | 6.25 | 2.279 | 0.497 | 2.641 | 2.729 | 0.665 | 0.180 | 1.491 |
| | 41-46 | 6.35 | 2.304 | 0.596 | 2.620 | 2.653 | 0.742 | 0.231 | 1.775 |
| Hallen Wood** | 51-53.5 | 6.01 | 2.166 | 0.706 | 3.981 | 2.653 | 0.925 | 0.953 | 1.135 |
| (Denchworth Series : | 53.5-56 | 6.43 | 2.465 | 0.471 | 2.200 | 2.950 | 0.712 | 0.980 | 1.112 |
| merging boundary | 56-58.5 | 6.66 | 1.297 | 0.364 | 1.541 | 2.087 | 0.388 | 0.757 | 0.925 |
| Worcester Series) | | | | | | | | | |
| Hallen Wood** | 58.5-61 | 7.30 | 0.513 | 0.326 | 1.128 | 1.334 | 0.234 | 0.606 | 0.753 |
| Denchworth Series*** | 0-20 | 7.71 | 1.528 | 0.301 | 0.272 | 0.828 | 0.401 | 0.155 | 1.107 |
| Evesham Series*** | 0-20 | 7.57 | 1.824 | 0.789 | 0.353 | 0.818 | 0.337 | 0.142 | 1.222 |

* : 1:2.5 fresh soil : deionised water extraction
** : 1 :2.5 air dried soil : deionised water extraction
*** : centrifuge drainage and immiscible liquid displacement methods as described by Kinniburgh and Miles 1983; data from Campbell *et al.*(1989) using fresh soil samples

equilibrium was attained under stable pH, and in order that the effect of microbial activity and anaerobic conditions were minimised. This ratio had also been used in assessment of the fresh soil pH. Using a more dilute 1:2.5 ratio would also draw greater conformity with the extracts used to determine heavy metal speciation within the two profiles. Table 4.4.17 provides information from this study and from the study by Campbell *et al.*(1989). All the soils belong to the Denchworth Series or related clay soil series e.g. subordinate soils of Denchworth Series can intergrade to Evesham Series (Findlay 1976). Campbell *et al.* (1989) compared their results with those of Larsen and Widdowson (1968) who used air dry soils which were rewetted and stored at 20°C for 2-53 days before soil solution extraction. The remarkable feature of the results of Larsen and Widdowson (1968) was the extremely high concentration of major solutes such as Ca, $NO_3$ and $SO_4$. Even after 2 days (the first sampling), sufficient N and S mineralisation had occurred to dominate the soil solution chemistry. Larsen and Widdowson compiled a table of earlier results of other authors (who had used rewetted soils) and these also showed similarly high concentrations. The results of this study (thesis) ratify the assessment that Campbell *et al.*(1989) make towards the results of Larsen and Widdowson. Furthermore, and perhaps more surprisingly, the results from Wetmoor, Haw Wood and Hallen Wood bear proximal association with the results of Campbell *et al* (1989) for Denchworth and Evesham Series soils (see Table 4.4.17). The pH of the samples of Campbell *et al.*(1989) were very high and the nearest that can compare were the bottom-most 58.5-61cm layer for Hallen Wood at pH7.30. In this layer, results for $NO_3$, Na, K and Ca are not dissimilar. Higher levels of Mg and $SO_4$ may well be the result of acidification processes that are taking place further up the Hallen profile. Indeed, for all sites ranging from pH6.01-7.71, $NO_3^-$ levels are remarkably similar and most of the $Cl^-$ results fall within the same order of magnitude. Without much stretch of the imagination, Wetmoor Wood $SO_4$ levels below 8.5cm depth (and perhaps slightly higher pH) would probably be in the same order of magnitude as the Denchworth/Evesham $SO_4$ levels found by Campbell *et al.*(1989). Clearly, levels of $SO_4$ in Haw Wood and Hallen Wood were higher (at depth) and further reiterate speculation that acid input to the Hallen / Haw Wood area in the form of $SO_x$ has perhaps occurred e.g. see Section 4.4.7 (this chapter). However, perhaps of more importance is that if the results of Campbell *et al.* (1989) are taken as representative of the "true" soil solution compositions of these soils at those pHs, then the results of air dry soil extraction of Haw Wood and Hallen Wood can perhaps be looked upon with a certain degree of

confidence as not being far from representing the "true" soil solution composition.

There are perhaps two principal reasons why the Haw and Hallen air dry soil solution compositions were not markedly different from the fresh soils of Campbell *et al.*(1989):

(a) The method of extraction was essentially rapid - shaking and filtering of soils was less than a day. Filtration occurred through natural forces rather than centrifugal, vacuum, pressure etc. forces. Allowing more "natural" infiltration / seepage to occur was perhaps little different to rewetting of a soil that has naturally become desiccated due to summer drought etc., although admittedly the ped/crumb structure of the air dried soil was different. The soils were also principally low in organic matter (mainly < 3% carbon) which might prevent active mineralisation by microbes occurring within the extraction time.

(b) In a study of the solution composition of wet and dry sites of the Denchworth soil series, Campbell *et al.*(1989) found that analysis of variance showed, somewhat surprisingly, that the only significant differences between wet and dry sites were that the soil solutions from the wet sites tended to have a higher alkalinity and a higher concentration of dissolved Sr. Otherwise, generally, the differences between the solution compositions at wet and dry sites were unlikely to be large and would probably not be seen against the other sources of variation.

It is also interesting to compare the results obtained by Sonneveld *et al.* (1990) for 1:2 extracts (where the suspension was shaken for 20 minutes and then filtered). The results of the Dutch, Haw Wood and Hallen Wood soils (to 26cm depth) are shown in Table 4.4.18. The standard deviations are given for Haw and Hallen soils in parentheses. Student's t-tests indicate that there were significant differences between the levels of K, Mg, Ca and $SO_4$ in the top 26cm of mineral soil in Haw Wood and Hallen Wood soils (confidence limit < 0.1%, n = 11). Haw Wood has more than twice the amount of Ca in solution (on average).

Table 4.4.19 indicates how much less easily exchangeable Ca there was in Hallen Wood. On average, there was 5 times less easily exchangeable Ca in Hallen Wood in relation to Haw Wood which was probably causal to the lack of Ca in the soil solution composition of Hallen Wood. Easily exchangeable Mg was only just significantly different between levels in Haw Wood and Hallen

**Table 4.4.18 Average Values and Ranges of Ionic Concentrations in Soil Solution 1:2 Extracts of Relatively Dry Greenhouse Soils (75 soils) from the Netherlands in Relation to Soil Solution 1:2.5 Extracts from Air Dry Haw Wood and Hallen Wood Soils (All soils from top 26cm of soil)**

| | Dutch Soils* (meq/l) | Haw Wood Soil (meq/l) | Hallen Wood Soil (meq/l) |
|---|---|---|---|
| Na | 3.4 (0.4 - 12.8) | 4.2 (±1.0) | 5.3 (±1.3) |
| K | 2.3 (0.1 - 5.9) | 2.7 (±1.8) | 6.0 (±1.3) |
| Mg | 0.9 (0.15 - 3.0) | 0.6 (±0.2) | 1.0 (±0.2) |
| Ca | 2.35 (0.4 - 7.2) | 3.4 (±1.3) | 1.5 (±0.4) |
| $NO_3^-$ | 5.4 (0.8 - 13.0) | 1.0 (±1.0) | 1.9 (±0.8) |
| $Cl^-$ | 2.6 (0.1 - 13.0) | 5.1 (±2.9) | 5.8 (±1.1) |
| $SO_4^{2-}$ | 2.3 (0.25 - 9.0) | 3.0 (±0.4) | 4.1 (±0.5) |

* : data from Sonneveld *et al.*(1990)

**Differences in the Chemical Composition of Hallen Wood and Haw Wood Soil Solutions**

| | Student's t-test Value |
|---|---|
| Na | 2.22‡ |
| K | 4.93* |
| Mg | 4.69* |
| Ca | 4.63* |
| $NO_3^-$ | 2.33‡ |
| $Cl^-$ | 0.75‡ |
| $SO_4^{2-}$ | 5.75* |

n = 11 * : $p < 0.1\%$ ‡ : not significant

**Table 4.4.19 Average Values and Standard Deviations of Easily Exchangeable (0.1M $NH_4NO_3$ extractable) Ca, Mg, Na and K in Haw Wood and Hallen Wood Soils to 26cm Depth**

| Metal | Haw Wood Soil (meq/100g) | | Hallen Wood Soil (meq/100g) | | Student's t-test Value |
|---|---|---|---|---|---|
| Ca | 1.372 | (±0.096) | 0.263 | (±0.065) | 31.7* |
| Mg | 0.190 | (±0.016) | 0.137 | (±0.038) | 4.3* |
| Na | 0.140 | (±0.012) | 0.079 | (±0.010) | 12.6* |
| K | 0.348 | (±0.112) | 0.320 | (±0.039) | 0.76‡ |

n = 11 * : $p < 0.1\%$ ‡ : not significant

---

Wood, whereas easily exchangeable K was not significantly different; and dissolution of these two metals within the top of the Hallen profile would appear to have been of importance to make up for any loss in Ca. Significantly higher levels of $SO_4^{2-}$ appeared to be associated with the change in the cation chemical composition of the soil solution in the topsoil of Hallen Wood in relation to Haw Wood. In Section 4.4.7 (this chapter), 9.0meq/l of $SO_4^{2-}$ were recorded in the fresh topsoil of Hallen Wood (Table 4.4.15) which is in the top of the range of levels of soluble sulphate recorded in the variety of soils studied by Sonneveld *et al.*(1990) (see Table 4.4.18). With the same respect, the levels of soluble K in Hallen Wood were also very high (Table 4.4.18), perhaps suggesting a high level of proton input to displace K from clays. Cooke (1981) stated that the amounts of cations that are lost by leaching depend on the amounts of water passing through the soil and on the anions present. Hence, if the solution must be electrically neutralised, then adding more soluble anions e.g. in the form of fertilisers (nitrate, chloride, sulphate), increases the loss of cations. In soils with clay minerals that can fix K, most of the increased loss falls on calcium (and sodium). In a similar way to that in which Cooke (1981) described these effects of fertiliser addition to a clay soil, one can perhaps relate a similar approach if additions to the Hallen soil were in the form $SO_x$ or $NO_x$ in acid deposition. Depletion of exchangeable metals, in terms of their t-values (see Table 4.4.19) within Hallen soil as compared to Haw soil followed the order:

$$Ca > Na > Mg > K$$

**Table 4.4.20**

| Depth (cm) | pH | Exch Ca+Mg meq/100g | Effective C.E.C. meq/100g | % Exch Ca+Mg Eff. C.E.C. |
|---|---|---|---|---|
| 0-1 | 4.35 | 0.3264 | 3.031 | 10.77 |
| 1-3.5 | 4.55 | 0.3771 | 2.946 | 12.80 |
| 3.5-6 | 4.37 | 0.3017 | 2.709 | 11.14 |
| 6-8.5 | 4.53 | 0.3341 | 2.445 | 13.66 |
| 8.5-11 | 4.55 | 0.3532 | 2.269 | 15.57 |

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This order of depletion follows Cooke's (1981) order of metal loss from clay soils and agrees with Polynov's (1937) order of metal mobility. It is important, however, to realise that this is based on the assumption that exchangeable levels of metals in Hallen Wood were originally similar to the levels in Haw Wood before the soil had been acidified to the state that it is presently in. Interestingly, soluble Mg significantly correlated best with soluble Ca ($r = 0.798$), more than with any other variable (see Section 4.4.6 this chapter) and hence the depletion of exchangeable Mg in the above order would appear to be too low in relation to Na. One likely source of "extra" exchangeable Mg in the top 26cm of soil could come from isomorphous substitution. Magnesium is just one of the metals found in the alumina octahedra of silicate clay minerals. In the Hallen profile (see Fig.3.6.10 Chapter 3 Section 6) acidification of the profile has led to an increase in the exchangeable levels of "acidic" cations such as Al, Fe, Mn and included the heavy metal Zn. Metals such as Al, Fe and Zn are all capable of isomorphous substitution with Mg in the octahedral sheets of clays such as montmorillonite, vermiculite, chlorite, talc etc. due to the similar sizes of their ionic radii (Brady 1984) which would help to provide extra Mg in an exchangeable form (and in solution form).

When exchangeable Ca and Mg are reduced to values below 5 to 10% of the effective cation exchange capacity of the soil then this is one indication that the aluminium buffer range of pH has been reached (Ulrich 1983). The pH at which a soil has entered the aluminium buffer range is pH4.2 or less (Ulrich 1983). Although using a different salt extractant to Ulrich and co-workers ($NH_4NO_3$ instead of $NH_4Cl$) and at a different strength (0.1M instead of 1M) (see Ulrich *et al.* 1980), the % easily exchangeable Ca and Mg in Hallen Wood appears to be low (see Table 4.4.20).

Both extractants rely on the $NH_4^+$ to displace the metal cations on exchange sites, and both extractants are neutral salts. It is quite possible that a 0.1M $NH_4NO_3$ extract would reflect the proportional amounts of metals extracted by a 1M $NH_4Cl$ extract. If this were so, then the above results would suggest that the topsoil of the Hallen profile was close to entering the aluminium buffer range as defined by Ulrich (1980, 1983, 1986), where dissolution of $Al^{3+}$ would be unlikely to occur on a large scale at or below pH4.2. Recording of pH in Hallen soil for 1979, 1984, 1985 and 1988 (see Chapter 2 Section 3) below pH4.2 indicates that the Hallen topsoil certainly has infringed within this buffer zone.

Fig.4.4.15 illustrates the Ca/Al ratio (molar basis) in the top 26cm of both woodland soils. Clearly the ratios were much higher in the Haw topsoil solution than in Hallen soil. Data for Al in Haw and Hallen topsoils to 26cm depth are given in Table 4.4.21.

The levels of soluble Al in the topsoils were not significantly different, and hence the low Ca/Al ratios in the Hallen soil solution could be attributable to the lack of Ca in solution. Nevertheless, low Ca/Al ratios of circa 1:1, e.g in 0-3.5cm depth in Hallen soil, are a cause for concern (e.g. Brown 1983, Huag 1984). Ulrich (1983) suggested that Ca/Al molar ratio in the soil solution below 1 (very critical below 0.2) can cause root injury. Any root injury, though, may not necessarily affect growth and above ground health of a plant or tree (Abrahamsen 1983, Skeffington 1983). Lacking better data, tentative acceptance of the German estimates is made that solution concentration ratios of less than 1:1 Ca/Al (or Ca/Mg) may impair roots (Binkley *et al.* 1989). Although the mean soluble Al concentration was higher in the Hallen topsoil, it was not significantly higher than the average Haw Al concentration. Of much more significance was the greater amount of exchangeable Al in Hallen Wood (see Table 4.4.21). The significantly lower exchangeable and soluble Ca, the significantly higher exchangeable Al, and yet the insignificantly higher soluble Al of Hallen topsoil in relation to Haw topsoil would suggest that Hallen topsoil was still within the cation exchange buffer range where exchangeable base cations play a deciding role in buffering acidification pushes (see Ulrich 1983); and yet also would suggest that aluminium buffering may already have been initiated.

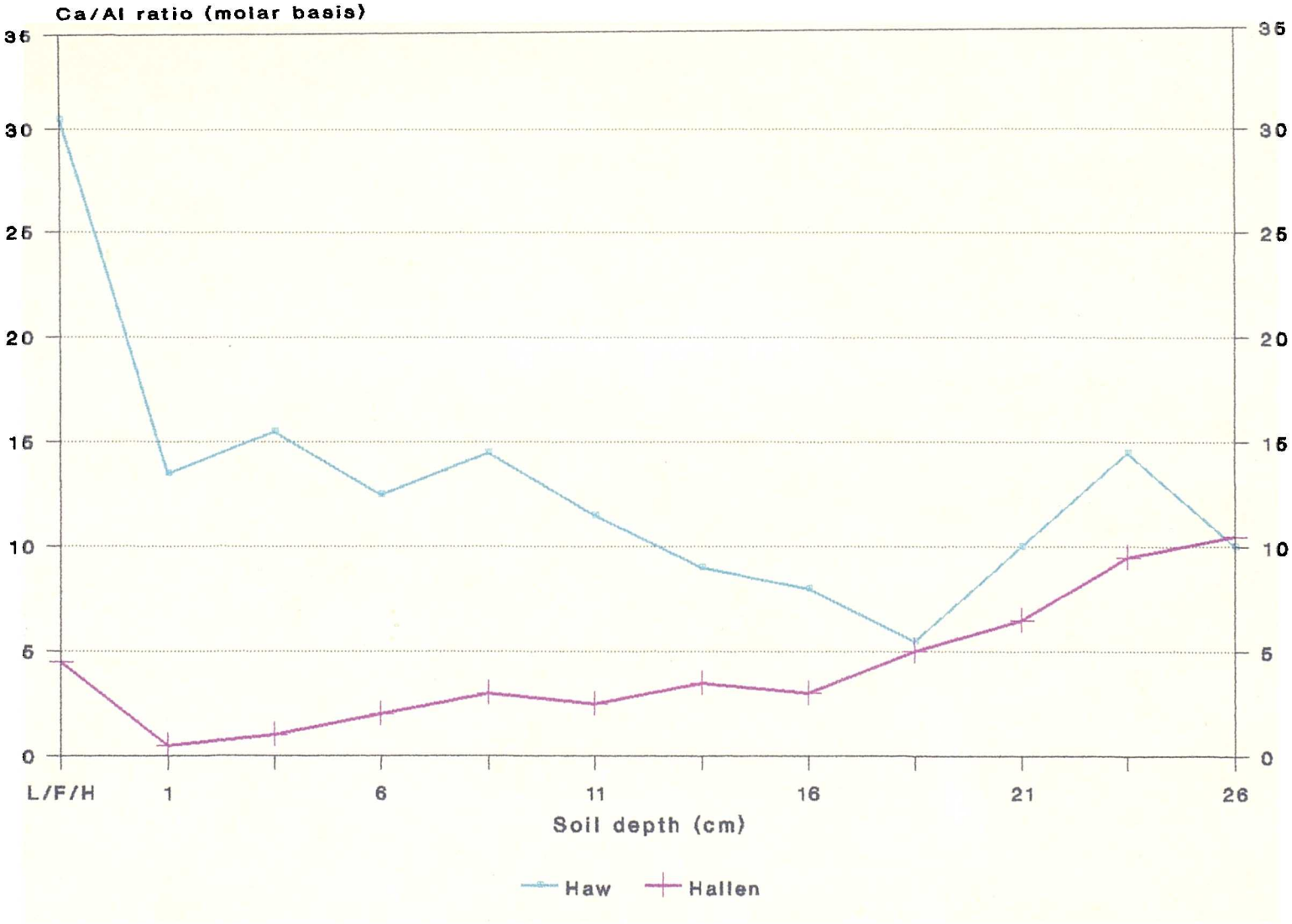


Fig.4.4.15 Ca/Al ratio in Haw and Hallen Wood water extracts.

**Table 4.4.21**

| | Haw Wood Soil | | Hallen Wood Soil | | Student's t-test Value |
|---|---|---|---|---|---|
| Soluble Al (meq/l) | 0.206 | (±0.076) | 0.357 | (±0.226) | 2.10‡ |
| Exchangeable Al (meq/100g) | 0.0021 | (±0.0007) | 0.0420 | (±0.0037) | 35.34* |

n = 11 * : $p < 0.1\%$ ‡ : not significant

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Certainly the pHs recorded in the Hallen 1988 topsoil, at pH values < 4.0, could potentially provoke the soil into releasing $Al^{3+}$ to compensate for any lack of base cations. Any periodic transgression of the soil pH into the range of pH that would stimulate Al buffering within that soil could inevitably have profound effects on the mobility and availability of a "low mobile" element such as Pb. Obviously from Chapter 2 Section 3 and Chapter 3 Section 6, Pb would appear to be relatively immobile in relation to heavy metals such as Cd and Zn. Any increase in the solubility of Al in solution would perhaps not only signify weathering of alumino silicates, but would also actively encourage isomorphous substitution of Al for Mg in some clay minerals. In a high clay content soil such as Hallen soil with higher levels of montmorillonite and chlorite (and illite), any substitution of $Al^{3+}$ for $Mg^{2+}$ would generate positive charges in octahedral sheets (similarly for $Fe^{3+}$ and $Mg^{2+}$) (Brown 1978, Brady 1984). Also at pHs below the point of net zero proton charge there is an increase in the number of positively charged sites on surfaces [$\equiv S\text{-}OH_2^+$] e.g. oxide and hydroxide surfaces (Evans 1989). The net result would be an increase in positive sites and possibly a reduction in the C.E.C. of the topsoil. Due to the high levels of Pb "stored" in the L, F, H layers of the Hallen profile, any further reduction in the soil pH below pH4.0 could start to see significant amounts of Pb move down the soil profile.

## 4.4.9. Discussion of Heavy Metal Speciation Results in the Soil Solution of Hallen Wood and Haw Wood Profiles

The results of the solution pH were not markedly different from the soil pH (see Fig.4.4.3 Section 4.4.3) which would support the suggestion that the

chemical composition of the soil solutions from fresh and air dry soils were relatively similar (see Section 4.4.8). The soil solution pH's were slightly reduced: a product of air drying the soil or a number of other factors such as setting up of a pH meter (Billet *et al.*1990). A number of reports demonstrate that originally air dried soils have been used in the speciation of heavy metals (e.g. Adams and Sanders 1985, Camerlynck and Kiekens 1982, Emmerich *et al.* 1982b, Jeffrey and Uren 1983, Sanders 1982, 1983) or else field-moist soils have been collected, stored and equilibrated at field capacity (e.g. McBride and Bouldin 1984, Tills and Alloway 1983a, 1983b, 1983c). Maintaining and extracting the "real" or "true" soil solution is a matter of contention. Even extracting soil solution from field-moist soils is not without difficulties and uncertainties, and no single extraction procedure is suitable for all types of soil or experimental conditions (Campbell *et al.*1989) (see also Section 4.4.8).

Table 4.4.22 illustrates how preliminary speciation results taken in 1987 reflected the results recorded later in 1988. Zn and Cu were in particular quite good. Cd was also good, except for the discrepancy shown in the F layer readings. Pb was also reasonable, with a little more variability in the results from deeper layers with lower Pb concentrations. Results in Sections 4.4.3 to 4.4.5 suggest that Cd and Zn were primarily found as cationic forms, Cu primarily occurred as anionic or low polar organic forms, and Pb was mainly found as cationic (in Hallen soil) and low polar organic / neutral forms (in Haw soil) within the woodland soils. Table 4.4.23 summarises data from four centres of heavy metal speciation research; this clearly illustrates that cationic forms of Cd and Zn tend to predominate in soil solutions. The Cd data for the Arizo soil (Sposito 1981 a) at pH8.2 is the one exception where Cd-cationic is only about 13% (83.5% as solid $CdCO_3$). Cu is primarily found in an organic form. Again, one exception to this is the data from Sposito (1981b) where organic Cu comprises only 8-18% of the soil solution composition. Hodgson *et al* (1966) and Jeffrey and Uren (1983) suggested that organic forms of Cu were an important form of Cu species. In calcareous soils, at least 99.5% of the Cu has been found to be in an organically complexed form (McBride and Bouldin 1984), and the likelihood is that as solution pH is raised, complexation between soluble humidified organic matter and Cu increases (Sanders and Bloomfield 1980).

The metal-organic complexes of liquid phases are very likely dominated by negatively charged species (Bloomfield *et al.*1976, Sims and Patrick 1978), and Tills and Alloway (1983a, 1983b, 1983c) suggested that anionic species in their scheme of metal speciation relate to more polar organic species. This

## Table 4.4.22 Speciation of Heavy Metals in Hallen Wood Soil Solution 1987/1988

% Speciation of Cadmium+

| Soil Depth (cm) | pH | Cationic | Anionic | Neutral | Low Polar Organics |
|---|---|---|---|---|---|
| F | 3.91 | 48.0 (74.0) | N.D. (2.30) | 22.1 (9.2) | 22.1 (14.5) |
| 0-1 | 4.36 | 74.7 (77.4) | 6.1 (4.9) | 6.1 (5.1) | 13.1 (13.6) |
| 8.5-11 | 4.53 | 76.2 (81.8) | 3.9 (2.1) | 8.9 (7.0) | 11.0 (9.0) |
| 18.5-21 | 4.77 | 85.3 (83.9) | 4.0 (4.2) | 5.0 (7.2) | 5.8 (4.7) |
| 28.5-31 | 5.10 | 85.4 (84.6) | 3.2 (2.6) | 4.0 (5.4) | 8.5 (7.4) |

% Speciation of Zinc+

| Soil Depth (cm) | pH | Cationic | Anionic | Neutral | Low Polar Organics |
|---|---|---|---|---|---|
| F | 3.91 | 86.2 (85.6) | N.D. (0.5) | 3.3 (2.5) | 10.5 (11.4) |
| 0-1 | 4.36 | 79.7 (78.2) | 3.8 (4.1) | 5.4 (5.7) | 11.1 (12.1) |
| 8.5-11 | 4.53 | 77.4 (79.5) | 8.6 (6.4) | 6.6 (6.3) | 7.4 (7.8) |
| 18.5-21 | 4.77 | 81.8 (76.4) | 6.0 (7.5) | 4.4 (8.6) | 7.7 (7.6) |
| 28.5-31 | 5.10 | 79.0 (76.3) | 5.5 (6.0) | 7.3 (7.8) | 8.2 (10.0) |

% Speciation of Lead+

| Soil Depth (cm) | pH | Cationic | Anionic | Neutral | Low Polar Organics |
|---|---|---|---|---|---|
| F | 3.91 | 60.7 (60.5) | 16.9 (15.8) | 2.8 (1.7) | 19.7 (21.9) |
| 0-1 | 4.36 | 45.0 (50.5) | 15.4 (13.3) | 14.3 (12.8) | 25.3 (22.4) |
| 8.5-11 | 4.53 | 32.3 (42.5) | 16.6 (8.1) | 22.6 (26.2) | 28.5 (23.3) |
| 18.5-21 | 4.77 | 24.0 (34.3) | 9.0 (23.6) | 24.3 (17.3) | 42.8 (24.8) |
| 28.5-31 | 5.10 | 25.9 (30.6) | 14.4 (20.8) | 28.5 (18.8) | 32.2 (29.9) |

% Speciation of Copper+

| Soil Depth (cm) | pH | Cationic | Anionic | Neutral | Low Polar Organics |
|---|---|---|---|---|---|
| F | 3.91 | 18.9 (16.4) | 43.8 (41.8) | 3.0 (5.3) | 34.3 (36.5) |
| 0-1 | 4.36 | 18.2 (19.7) | 38.3 (37.8) | 8.6 (8.9) | 34.8 (33.5) |
| 8.5-11 | 4.53 | 26.3 (18.8) | 38.4 (42.3) | 8.8 (9.7) | 26.5 (29.2) |
| 18.5-21 | 4.77 | 31.4 (17.0) | 29.0 (35.0) | 10.5 (12.6) | 29.2 (35.3) |
| 28.5-31 | 5.10 | 37.7 (31.0) | 20.5 (22.8) | 12.5 (13.5) | 29.5 (32.7) |

+ : 1987 figures outside parentheses 1988 figures inside parentheses

**Table 4.4.23** **Heavy Metal Speciation in Soil Solutions**

Group A : Sposito and Co-workers, University of California, U.S.A.

| Soils | pH | Principal Species (% distribution in parentheses) | | | References |
|---|---|---|---|---|---|
| Calki+ | 6.40 | Cadmium | : Cationic (65-86%) | Neutral (7-21%) | Sposito (1981 a, b, 1983) |
| Ramona+ | 5.2-6.7 | | Organic (<1-21%) | | |
| Redding+ | 4.8-5.6 | Copper | : Cationic (<1-59%) | Neutral (<1-52%) | Mahler *et al.*(1980) |
| San Miguel+ | 5.1-5.2 | | Organic (41-100%) | | Mattigod (1981) |
| Hanford+ | 5.4-5.7 | Zinc | : Cationic (61-78%) | Neutral (12-35%) | Emmerich *et al.* (1982) |
| Arizo+ | 8.2 | | Organic (<1-12%) | | |
| Domino+ | 7.6 | | | | Sposito & Bingham (1981) |
| Alkamount* | 6.9 | | | | |
| Holtville* | 7.6-7.9 | | | | Bingham *et al.*(1984) |

Principal Species in Acidic Soils (Sposito 1983)

Cadmium : $Cd^{2+} > CdSO_4^\circ > CdCl^+$
Copper : Cu-organic > $Cu^{2+}$
Lead : $Pb^{2+}$ > Pb-organic > $PbSO_4^\circ > PbHCO_3^+$
Zinc : $Zn^{2+} > ZnSO_4^\circ$

\+ : sandy/loamy soils
* : clay soils (predominantly treated with sewage sludge, waste water etc.)

Group B : Tyler and Co-workers, University of Lund, Sweden

| Soils | pH | Principal Species (% distribution in parentheses) | | | References |
|---|---|---|---|---|---|
| Brown forest soils - probably sandy-silt (see Tyler 1981, Bergkvist 1986 1987) | 4.0-5.5 | Cadmium : Cationic (54-87%) | Neutral (3-5%) | | Tyler *et al.*(1987) Bergkvist & Folkeson (1988) Bergkvist *et al.* (1989) Berggren (1989) |
| | | Organic (8-43%) | | | |
| | | Copper : Cationic (3-22%) | Neutral (<1-1%) | | |
| | | Organic (76-97%) | | | |
| | | Lead : Cationic (6-37%) | Neutral (<1-3%) | | |
| | | Organic (60-93%) | | | |
| | | Zinc : Cationic (93-95%) | | | |



Group C : Tills and Alloway, University of London, U.K.

| Soils | pH | Principal Species (% distribution in parentheses) | | | References |
|---|---|---|---|---|---|
| A range of polluted soils (mainly treated with sewage sludge/mining activity) | 3.90-8.20 | Cadmium : Cationic (54-99%) | Neutral (<1-36%) | | Tills & Alloway (1983 a, b, c) |
| | | Anionic (<1-8%) | Organic (<1-6%) | | |
| | | Lead : Cationic (27-99%) | Neutral (<1-68%) | | |
| | | Anionic (<1-8%) | Organic(<1-10%) | | |

Group D : Adams and Sanders, Rothamsted Experimental Station, U.K.

| Soil Series | pH | Principal Species (% distribution in parentheses) | References |
|---|---|---|---|
| Marcham+ | 4.75-7.45 | Copper : Free Ion (<1-31%) $Cu^{2+}$ | Adams & Sanders |
| Cottenham+ | 6.2-7.6 | Zinc : Free Ion (21-100%) $Zn^{2+}$ | (1985) |
| Newport+ | 7.0-7.9 | | Sanders (1982) |
| Carswell* | 6.3-7.5 | | Sanders (1983) |
| Upton | 7.3-7.9 | | |

+ : sandy/loamy soils
* : clay soils

**Table 4.4.24 The % Organic Species of Heavy Metals in the Haw Wood and Hallen Wood Topsoil Solutions**

| Metal | % Organic Species (anionic + low polar organics) Haw 0-11cm Depth | Hallen 0-11cm Depth |
|---|---|---|
| Cd | 24.8 (±7.1) | 11.7 (±4.0) |
| Cu | 90.9 (±3.4) | 73.1 (±3.1) |
| Pb | 63.0 (±5.7) | 31.2 (±5.0) |
| Zn | 21.2 (±7.8) | 12.4 (±3.1) |

Standard deviation in parentheses

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makes a lot of sense as no principal inorganic species of Cd, Cu, Pb and Zn is of an anionic nature (see Table 4.4.23), which would appear to be especially true of acidic soils (see Sposito 1983). The anionic nature of an organic complexant such as EDTA binding on Zn was effectively demonstrated by Camerlynck and Kiekens (1982). Table 4.4.24 shows the % of organic species of the four metals in the topsoils of both woodlands. Clearly a greater proportion of species in the Haw soil solution were organo-metallic species in relation to Hallen topsoil solution. This was probably the result of:

(a) The higher % C in the Haw Wood topsoil layers in relation to the % C recorded for Hallen topsoil (see Chapter 2 Section 3).

(b) Acidification lowering the pH of Hallen soil solutions. This could decrease the concentration of dissolved organic matter in soil solutions (Jacks *et al.* 1984). The aggregation of humic acids and fulvic acids occurs at low pH which can be explained by hydrogen bonding, van der Waal's interactions, and interactions between $\Pi$ electrons of adjacent molecules, as well as homolytic reactions between free radicals; but as the pH of a solution increases, these forces become weaker, and because of increasing ionisation of carboxylic acid and phenolic hydroxyl groups, particles separate and begin to repel each other electrostatically, so that the molecular arrangements become smaller (Schnitzer 1980).

Thus a greater quantity of dissolved organic matter and perhaps increased quantity of humic acids in Haw Wood soil would help partially explain the differences in Table 4.4.24. However, there is perhaps another consideration

## Table 4.4.25 Stability Constants of Metal-Fulvate Complexes (after Schnitzer and Hansen 1970)

CV : Continuous variations method
IE : Ion-exchange equilibrium method

Log K (stability constants)

| Metal | pH3.0 CV | pH3.0 IE | pH5.0 CV | pH5.0 IE |
|---|---|---|---|---|
| $Cu^{2+}$ | 3.3 | 3.3 | 4.0 | 4.0 |
| $Ni^{2+}$ | 3.1 | 3.2 | 4.2 | 4.2 |
| $Co^{2+}$ | 2.9 | 2.8 | 4.2 | 4.1 |
| $Pb^{2+}$ | 2.6 | 2.7 | 4.1 | 4.0 |
| $Ca^{2+}$ | 2.6 | 2.7 | 3.4 | 3.3 |
| $Zn^{2+}$ | 2.4 | 2.2 | 3.7 | 3.6 |
| $Mn^{2+}$ | 2.1 | 2.2 | 3.7 | 3.7 |
| $Mg^{2+}$ | 1.9 | 1.9 | 2.2 | 2.1 |
| $Fe^{3+}$ | 6.1* | - | - | - |
| $Al^{3+}$ | 3.7** | 3.7** | - | - |

* : determined at pH1.70
** : determined at pH2.35

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## Table 4.4.26 % Composition of Soil Solutions to 16cm Depth Recorded in Haw, Hallen and a S. Swedish Woodland Mineral Soil

| Element | Haw Wood | Hallen Wood | S. Sweden (birch wood) |
|---|---|---|---|
| $Ca^{2+}$ | 31.8 | 10.1 | 6.6 |
| $Mg^{2+}$ | 5.3 | 6.7 | 2.9 |
| $K^{+}$ | 26.6 | 40.1 | 45.8 |
| $Na^{+}$ | 36.3 | 43.1 | 44.7 |
| $Cl^{-}$ | 49.5 | 46.7 | 37.8 |
| $SO_4^{2-}$ | 24.1 | 27.9 | 22.6 |
| $NO_3^{-}$ | 11.1 | 12.7 | 0.72 |
| $Org^{-}$* | 15.3 | 12.7 | 38.8 |

* : organic complexants calculated from equivalent charge difference for all three soils (see Section 4.8)

to take into account. Table 4.4.25 illustrates the stability constants of metals with fulvic acids. There are two important things to note about the data in this table:

(a) The stability constants of $Cu^{2+}$ ,$Pb^{2+}$ and $Zn^{2+}$ (and presumably $Cd^{2+}$) increase with an increase of pH from pH3.0 to pH5.0.
(b) The stability constants of $Pb^{2+}$ and $Cu^{2+}$ are similar at pH5.0, whereas at lower pH, pH3.0, the stability constants of $Pb^{2+}$ are more akin to $Ca^{2+}$ (and indeed $Zn^{2+}$) than they are to $Cu^{2+}$.

Interestingly the pHs of the Hallen and Haw soil solutions in the topsoil, 0-11cm, were pH4.32-pH4.50 and pH5.00-pH5.90 respectively. Such factors might be important in explaining why all four metals (Cd, Cu, Pb and Zn) have a higher proportion of organic complexes in the Haw topsoil and also why a metal such as Pb had a much greater proportion of cationic species in the Hallen soil than in the Haw soil.

In a study by Berggren (1989) on a brown forest soil in a birch (*Betula pendula*) stand in S.Sweden, soil solution was collected from a 15cm deep percolation lysimeter. The pH of the "natural" soil solution was adjusted up to pH5.5 with 0.1M NaOH and down to pH4.0 with 0.1M $HNO_3$. The solution composition of the Swedish soil (15cm) and the Haw/Hallen soils (to 16cm depth) are shown in Table 4.4.26. Unfortunately the original pH of the birch wood soil solution (Sweden) was not given, but earlier data from Berggren (see Tyler *et al.*1987) suggested that the pH of the acid forest soil solutions was *circa* pH4.6. Although in terms of equivalents the Haw and Hallen soils did not reflect the Swedish soil, in terms of % composition the Hallen soil solution showed some similarity to the Swedish data. The Swedish soil, however, appeared to have a greater proportion of organic constituents and lower nitrate. Table 4.4.27 provides the % speciation of heavy metals in the soil solutions.

Despite the likely heavier nature of the Haw and Hallen soils in terms of % clay / silt fraction (generally > 75% in Denchworth Series soils, Findlay 1976) in relation to the Swedish soil, there were still sufficient organic complexes to affect the speciation of Cu in both Haw Wood and Hallen Wood soils. The importance of humic substances providing complexant ligands for heavy metals in woodland / forest soil solution was stressed by Berggren (see Bergkvist and Folkeson 1988, Bergkvist *et al.*1989).

**Table 4.4.27 Speciation of Heavy Metals Cd, Cu, Pb and Zn in Woodland/Forest Soil Solutions of Haw Wood, Hallen Wood and a S. Swedish Woodland, in the Top 15-16cm of Mineral Soil**

Southern Sweden (*Betula pendula* woodland)

| Element | % Cationic | % Neutral | % Organic | Solution pH |
|---|---|---|---|---|
| Cu | 12.1 (±7.0) | 0.7 (±0.4) | 87.2 (±7.3) | 4.0-4.5 |
| Cu | 6.1 (±2.6) | 0.3 (±0.1) | 93.6 (±2.8) | 5.0-5.5 |
| Pb | 23.3 (±9.0) | 2.2 (±0.8) | 74.6 (±9.8) | 4.0-4.5 |
| Pb | 10.2 (±3.0) | 0.9 (±0.3) | 88.9 (±3.4) | 5.0-5.5 |
| Cd | 83.8 (±1.8) | 4.7 (±0.3) | 11.5 (±1.8) | 4.0-4.5 |
| Cd | 68.6 (±8.2) | 3.7 (±0.7) | 27.7 (±8.8) | 5.0-5.5 |

Haw and Hallen (*Quercus robur / Corylus avellana* woodland)

| Element | % Cationic | % Neutral | % Organic | Solution pH |
|---|---|---|---|---|
| Cu | 15.4 (±4.5) | 10.0 (±4.0) | 74.6 (±4.8) | 4.5-4.5* |
| Cu | 0.7 (±1.0) | 8.3 (±4.2) | 90.9 (±3.4) | 5.0-5.9‡ |
| Pb | 45.3 (±11.1) | 19.6 (±5.1) | 34.9 (±8.7) | 4.3-4.5* |
| Pb | 4.6 (±4.0) | 32.4 (±5.2) | 63.0 (±5.7) | 5.0-5.9‡ |
| Cd | 82.9 (±5.9) | 7.0 (±4.4) | 10.2 (±4.5) | 4.3-4.5* |
| Cd | 52.9 (±8.1) | 22.4 (±1.7) | 24.8 (±7.1) | 5.0-5.9‡ |
| Zn | 80.2 (±5.9) | 6.4 (±2.5) | 13.4 (±3.9) | 4.3-4.5* |
| Zn | 64.0 (±9.9) | 14.7 (±2.3) | 21.2 (±7.8) | 5.0-5.9‡ |

* : Hallen Wood ‡ : Haw Wood

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However, it is interesting to note that in the Swedish study, inorganic complex ligands play a relatively minor role in heavy metal speciation (Berggren 1989, Bergkvist and Folkeson 1988, Bergkvist *et al.*1989). In Haw and Hallen soils, neutral complexes (see Table 4.4.27) form a more significant fraction of the speciation of Cd, Cu, Pb and Zn. The sulphate ligand is important in the formation of neutral complexes (see Sposito 1983) of heavy metals in soil solutions, and calculations using SOLMINEQ 88 suggest that it was the

sulphate ligand that forms the neutral species in Haw / Hallen soil solutions (see Section 4.4.10). This emphasises the fact that the Haw/Hallen soil solutions had less dissolved organic carbon in relation to Swedish soils and/or the levels of sulphate in the former soil solutions were sufficiently higher than the latter.

Bergkvist *et al.*(1989) drew the following conclusions about the speciation of Cu, Pb and Cd in humic substance-containing solutions from a brown forest soil:

(a) Organic ligands (humic substances) were the most important ligands for all metals studied.
(b) The strength of complexes formed between the humic substance and the metals decreased in the order:

$$Cu > Pb \gg Cd$$

(c) The relative importance of humic complexation on the speciation increased greatly with pH and concentration of humic substances.
(d) The proportion of metal complexed to humic substances increased as the metal to humic substances ratio decreased.

They suggested that Zn speciation would behave similarly to Cd speciation. As regards Haw/Hallen topsoils, conclusion (a) is likely to be true for Cu, Pb and Zn, but there is the possibility that inorganic complexants would form a greater proportion of Cd species due to the formation of $CdCl^+$. Results from Hallen/Haw soil solutions support conclusion (b) and it is suggested that the order of strength of complexation between metals and organic ligands was:

$$Cu > Pb \gg Zn = Cd$$

Haw Wood soil had higher pH and % carbon values in relation to Hallen Wood soil and this would lend some support to conclusion (c).

The majority of soils used in published studies of heavy metal speciation in soil solutions have tended to be of a sandy loam nature. There are very few examples of soil solutions used from woodland soils. Apart from one example from Germany (König and Ulrich 1986) and the Swedish studies (Tyler and co-workers in Table 4.4.23), no other studies appear to have looked at woodland/forest soil solutions. Hallen / Haw soils were both heavy clay

woodland soils and data collected from these two sites add new information about a subject that is still very much in its infancy. It is important to stress that the combination of high bioavailability and a high proportion of cationic forms (principally free ions, $M^{2+}$) of metals such as Zn and in particular Cd, could have potentially harmful implications for biological processes within the soils. The fact that Cd and Zn were predominantly cationic in Haw and Hallen soils is a feature of the greater mobility of these two metals within the soils.

## 4.4.10. Calculating the Chemical Speciation of Heavy Metals in the Soil Solution using SOLMINEQ 88

SOLMINEQ 88 PC/SHELL is a user-friendly, menu driven program which allows the user to easily reduce water analyses to meaningful quantities and to model geochemical reactions. It includes full screen data entry with error checking, graphical analysis and user interactive control (Wiwchar *et al.*1988). SOLMINEQ 88 PC/SHELL is based on the PC version of the computer code SOLMINEQ 88 (Kharaka *et al.*1988). One of its many applications includes chemical speciation in water.

Unfortunately, of the metals of interest, the system only considers $Zn^{2+}$ and $Pb^{2+}$. $Cd^{2+}$ is not considered, and copper is only available as the $Cu^{+}$ form. Results for Hallen Wood and Haw Wood are summarised in Table 4.4.28. The data in this table illustrate that an element such as Zn was least affected by organic ligands and hence the "analytical results" obtained by the ion-exchange procedure tended to comply with those obtained from the SOLMINEQ 88 "predicted" results for cationic and neutral species, although neutral species in Hallen soil were significantly different. Pb analytical results differed from the computer predicted results, more so in the Haw soil than in the Hallen soil. This is perhaps indicative of the relatively influential effect that organic ligands have on Pb in the higher pH topsoil solution of Haw Wood. The computer predicted results suggest that inorganic ligands, in particular sulphate, play an important role in the complexation of Zn and Pb - hence the high proportion of neutral species both predicted by the computer and recorded analytically. The fact that both methods reflect a relatively high proportion of neutral species is encouraging. Swedish workers (Bergkvist and Folkeson 1988, Bergkvist *et al.* 1989) suggested that even without the influence of organic ligands, 4% or less of heavy metal species for Cd, Cu, Pb and Zn occurred as neutral species. This demonstrates the relative importance of the sulphate ligand in Hallen Wood and Haw Wood soil solutions with respect to the abundance of organic ligands.

## Table 4.4.28 Proportion of Heavy Metal Species of Zn and Pb in Hallen Wood and Haw Wood Soil Solutions

Hallen Wood Zinc : n = 22

| | Cationic | Neutral | Anionic |
|---|---|---|---|
| Analytical (ion-exchange) | 76.13 (±6.27) | 9.39 (±4.33) | 6.21 (±3.41) |
| Predicted (SOLMINEQ 88) | 73.59 (±3.59)‡ | 18.14 (±1.89)** | <0.01 |

Hallen Wood Lead : n = 22

| | Cationic | Neutral | Anionic |
|---|---|---|---|
| Analytical | 44.84 (±11.77) | 23.67 (±9.65) | 9.40 (±8.18) |
| Predicted | 53.06 (±6.98)* | 24.90 (±2.61)‡ | <0.01 |

Haw Wood Zinc : n = 6

| | Cationic | Neutral | Anionic |
|---|---|---|---|
| Analytical | 68.01 (±13.12) | 12.82 (±5.14) | 8.90 (±4.33) |
| Predicted | 76.67 (±5.15)‡ | 13.06 (±1.62)‡ | <0.01 |

Haw Wood Lead : n = 6

| | Cationic | Neutral | Anionic |
|---|---|---|---|
| Analytical | 10.66 (±15.32) | 28.72 (±10.10) | 21.07 (±10.74) |
| Predicted | 47.21 (±11.42)** | 13.25 (±2.87)** | <0.01 |

* : $p < 5\%$ ** : $p < 1\%$ ‡ : not significant t values

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The compatibility between predicted and analytical results for Zn (see Fig.4.4.16), although not perfect, is still good enough to provide a degree of confidence in the analytical results that have been obtained. The results for Pb were not as good as for Zn, but nevertheless, apart from the mid-profile, a similar trend between analytical and predicted results was still maintained. The likelihood is that if $Cd^{2+}$ and $Cu^{2+}$ were available on the computer program, then Cd analytical and predicted results would compare favourably, whereas Cu analytical and predicted results would not compare very well due to the modifying effect of Cu-organo complexes in the analytical results.

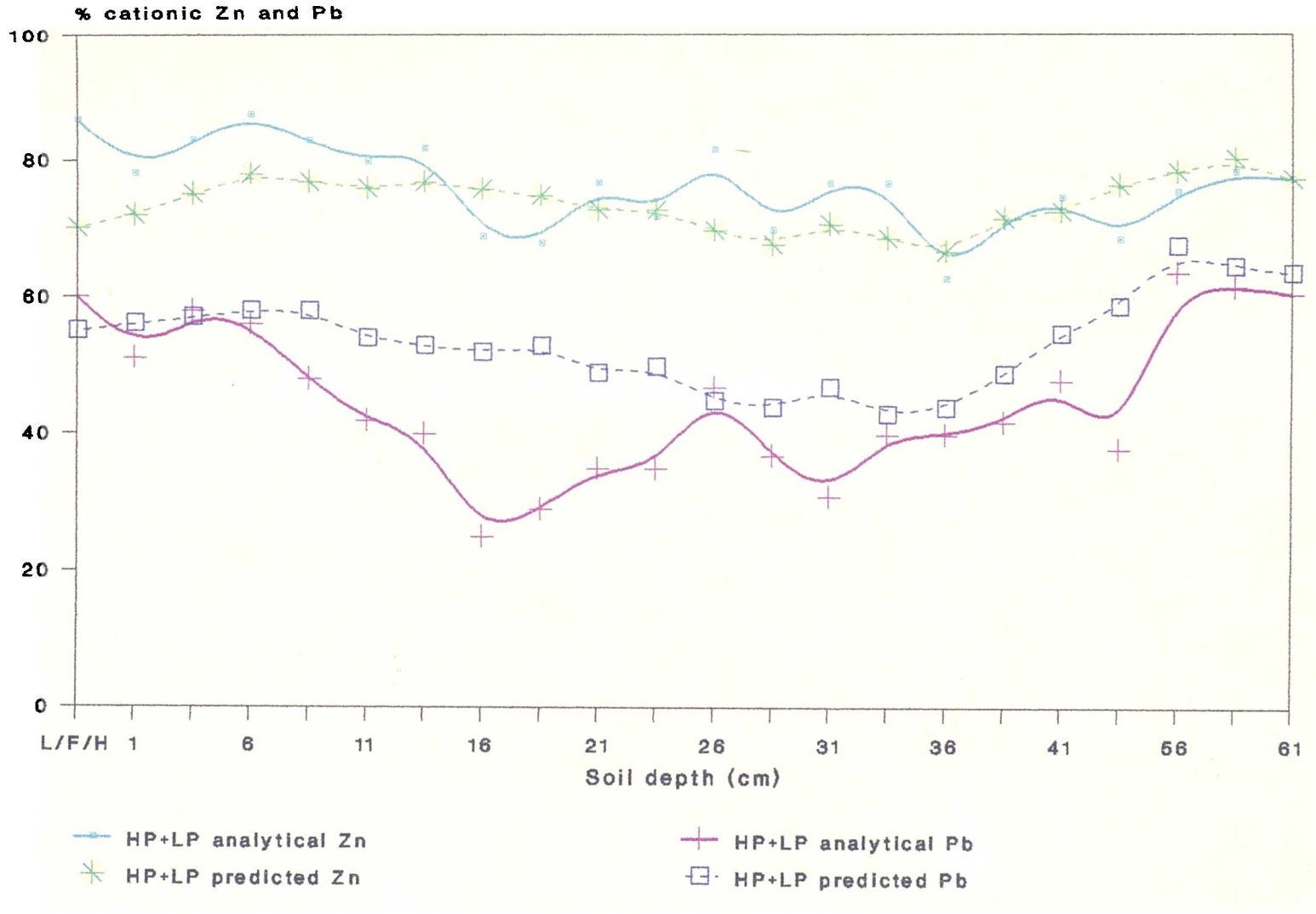


**Fig.4.4.16 Zinc and Lead Cationic Species: Hallen Wood soil.(HP=high polar, LP=low polar species).**

Using the combination of computer and analytical ion-exchange / chromatographic procedures, the principal heavy metal species present within the Hallen/Haw soil solutions would appear to be in the order:

Hallen Zn : $Zn^{2+}$ » Zn-organics = $ZnSO_4^\circ$ » $ZnCl^+$
Haw Zn : $Zn^{2+}$ » Zn-organics = $ZnSO_4^\circ$ » $ZnCl^+$ > $ZnOH^+$

Hallen Pb : $Pb^{2+}$ > Pb-organics > $PbSO_4^\circ$ » $PbCl^+$ > $PbOH^+$
Haw Pb : Pb-organics > $PbSO_4^\circ$ » $Pb^{2+}$, $PbCl^+$, $PbOH^+$

From the studies in Table 4.4.23 and from the chemical nature of Cd and Cu, it is suggested that the likely speciation of these two metals follow the order:

Hallen Cd : $Cd^{2+}$ » Cd-organics, $CdSO_4^\circ$, $CdCl^+$
Haw Cd : $Cd^{2+}$ > Cd-organics, $CdSO_4^\circ$ > $CdCl^+$ > $CdOH^+$

Hallen Cu : Cu-organics > $CuSO_4^\circ$, $Cu^{2+}$ » $CuCl^+$
Haw Cu : Cu-organics » $CuSO_4^\circ$ > $Cu^{2+}$, $CuCl^+$, $CuOH^+$

Due to the "soft" nature of Cd, the complex $CdCl^+$ would be more prevalent than the chloro-complex is for the other three metals. There is the possibility that the $CdCl^+$ complex would be more important than is suggested in the order for Haw soil. This would reduce the importance of the free $Cd^{2+}$ ion in the soil solution which might have biological/plant uptake implications; although a reduction of $Cd^{2+}$ in relation to an increase in $CdCl^+$ may encourage plant uptake of Cd (Sposito and Bingham 1981). Interestingly, if Cu is considered in the reduced form, $Cu^+$, then the principal species of the "soft" form of $Cu^+$ is anionic $CuCl_2^-$ (not taking organic ligands into account).

## 4.5. Summary and Conclusions

(a) The soil solution is a natural, dynamic, open water system. Heavy metal ions in solution generally behave as Lewis acids because they have vacant orbitals which can accept electrons. In solution they exist chemically either as free (uncomplexed) ions or as a range of complexes with both inorganic and organic ligands. Ecologically, the concentrations and forms of heavy metal species in solution are of immense importance because metal mobility and availability are closely related to the composition of the liquid phase.

(b) The problem of obtaining the "true" soil solution has not yet been solved. Methods used to extract the soil solution and determine the metal species within the liquid phase all tend to have their own form of inherent problems. Despite any drawbacks, ion exchange techniques and computer modelling studies appear to be used frequently and have proved very useful in evaluating metal speciation in aqueous systems.

(c) Changes in soil pH can affect heavy metal solubility. Controlled pH adjustments of soil / peat suspensions (in deionised water) illustrated that heavy metal solubility was enhanced with a decrease in suspension pH. The solubility of Cd and Zn was enhanced in relation to Cu and Pb.

(d) Soluble Cd and Zn species within Hallen and Haw soil solutions occurred primarily in a cationic form. Soluble Cu species were principally found as low polar organic and anionic forms within the Hallen soil solution, whereas anionic Cu species were dominant within the Haw soil solution. Pb speciation was a little more mixed with cationic forms being more important within the Hallen soil solution, whereas low polar and neutral species were perhaps of more significance in the Haw soil solution.

(e) With respect to other studies, the anionic / cationic compositions of the Haw and Hallen soil solutions did not appear to be unreasonable. Furthermore analytical / computer predicted heavy metal speciation results for Haw and Hallen soil solutions compared reasonably well with other similar studies.

# CHAPTER FIVE

# THE ECOLOGICAL CONSEQUENCES OF HEAVY METAL AVAILABILITY WITHIN THE HALLEN AND HAW WOOD SOIL PROFILES

## 5.1. Introduction

In Chapter 3, Section 4.6 it was mentioned that the availability of metals such as Cd and Zn in the Hallen soil profile could have repercussions upon biological activity within the soil. Relating soil heavy metal availability to plant uptake and biological activity is not an easy process. With respect to plants, their chemical composition generally reflects the elemental composition of the growth media, although the extent to which this relation exists is highly variable and is governed by many different factors (Kabata-Pendias and Pendias 1984). Within this Chapter, two aspects of metal availability are looked at in relation to:

(a) The available Cd, Cu, Pb and Zn in the Hallen and Haw Wood profiles and uptake by the grass *Holcus lanatus.*
(b) The impact of acidification of soil on the uptake of Cd, Cu, Pb and Zn by the sunflower, *Helianthus annuus.*

## 5.2. Availability of Heavy Metals in Soils and Plant Uptake.

Several factors should be taken into account when considering plant heavy metal uptake in the plant-soil system. Brümmer (1986) has emphasised three important factors (Fig.5.2.1 after Brümmer 1986 and West 1981):

(a) Quantity - the available elemental pool in the soil.
(b) Intensity - the activity of an element in the soil solution.
(c) Rate - maintenance of equilibrium between (a) and (b).

Another factor to consider is the Capacity factor which represents a fraction which may become plant available during plant growth (Kiekens and Cottenie 1985). Kabata-Pendias and Pendias (1984) have pointed to numerous factors that affect absorption of trace elements by plant roots. In addition to Fig.5.2.1, they suggest that:

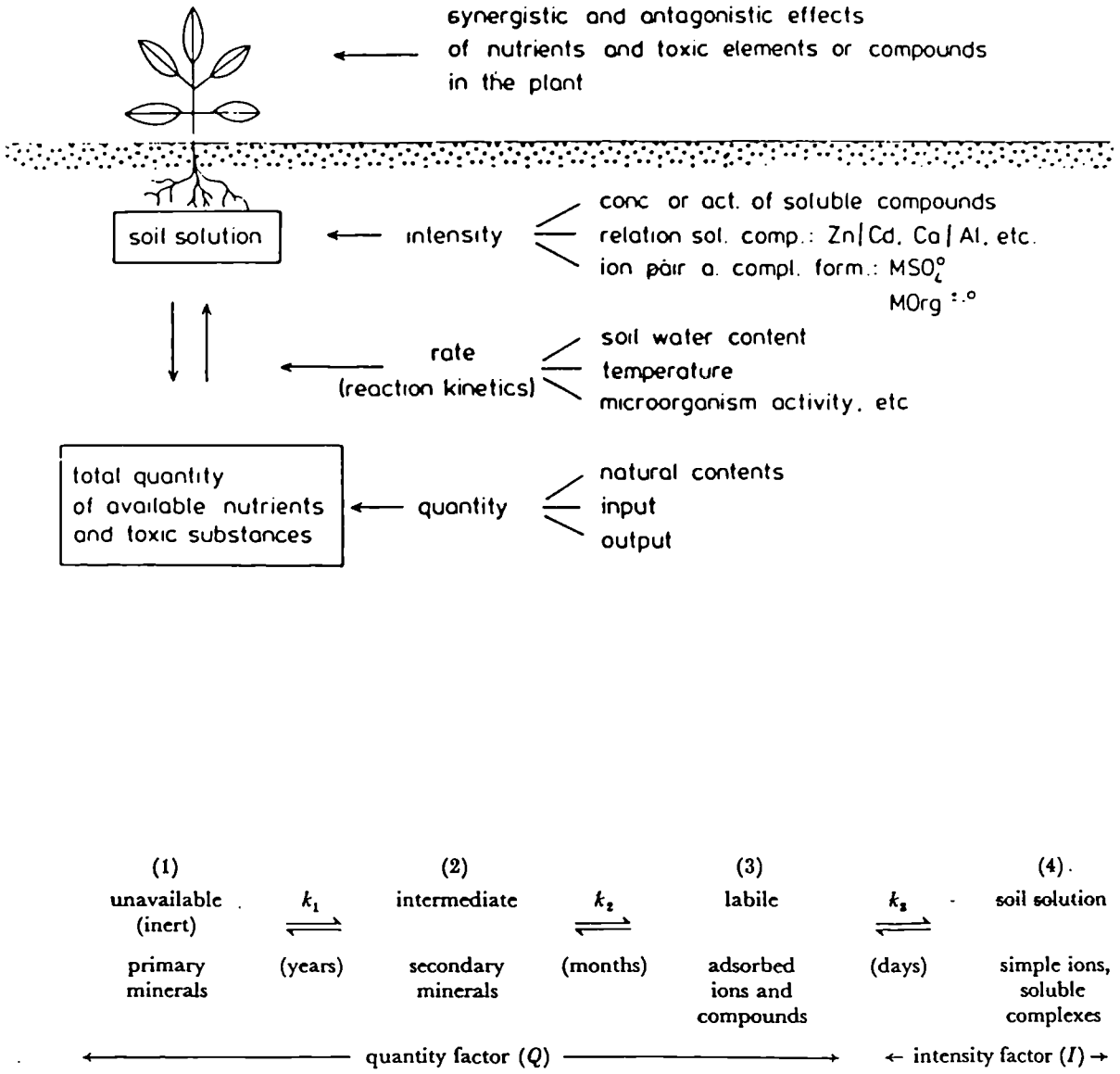


Fig.5.2.1 Schematic presentation of the parameters which determine the availability of heavy metals for plants

(a) The rate depends strongly on the occurrence of $H^+$ and other ions.
(b) The intensity varies with plant species and it's stage of development.

The two principal processes involved with the transfer of solutes from soil to plant in the soil solution are (Jones and Jarvis 1981):

(a) Mass flow - with the soil solution as it moves to and is absorbed by the root.
(b) Diffusion - through the soil solution down the concentration gradient created by the absorption of ions by the root.

Plant root uptake of solutes is either a passive (non-metabolic) or an active (metabolic) process. Passive uptake involves the diffusion of nutrients from the external soil solution into the root endodermis. Active uptake requires the use of metabolic energy for absorption against a chemical gradient.

The aforementioned principal factors and processes occur within the broad framework of the plant-soil system. In trying to understand the availability to plants of heavy metals in soils, it is important to be aware of the primary reactants within the system (i.e. the plant environment, the soil environment and the nutrients/elements of interest).

Uptake of metals into the plant system is not restricted to the roots as foliar uptake from aerial deposits can occur. However, in view of the experimental work in this Chapter, the principal emphasis is on root uptake, mainly from contaminated soils. It is also worth reiterating that metals such as Cd and Pb are considered to have no biological function and at high concentrations can be toxic to plants. However, Zn and Cu are essential trace elements which serve biological functions in plants, and hence have upper toxic threshold limits and lower deficiency threshold limits in plants. Attention is also drawn to the fact that, whilst recognising the importance of roots in uptake of heavy metals into plants from soils, much of the emphasis is placed on metal accumulation, tissue concentrations and toxicity to the aerial parts of plants. For, although roots might be more sensitive indicators of soil toxicity than concentration in shoots, even very slight soil contamination can have a disproportionately large effect on root analyses; especially as it is usually difficult to completely free roots from soil (MacNicol and Beckett 1985).

## 5.2.1. Soil Factors Affecting Metal Availability to Plants

Numerous soil factors are important in governing heavy metal uptake in plants. Hughes *et al.* (1980) tabulate information concerning pH, organic matter and CEC from a vast wealth of literature mainly published in the 1970's. One of the most important factors influencing immobilisation of heavy metals in soil is pH (Jarvis 1977). It is suggested that one of the main factors influencing whole plant uptake of heavy metals is also soil pH (Davies 1980, Hughes *et al.* 1980). Soil pH has been shown to exert a strong influence on Cd availability (Mahler *et al.* 1980) which is probably one of the most readily available trace elements to plants in soil-plant systems (Kabata-Pendias and Pendias 1984). In order to minimise plant uptake and potential toxicity problems, soil / sludge pH's are recommended to exceed pH6.5 (Bolton 1975, Jarvis 1977, Kuo *et al.* 1985). The decrease in availability and uptake with increasing soil pH values of 6.5 or more is of particular importance for a potentially toxic element such as Cd (Thornton and Webb 1980). In general crops tend to absorb greater quantities of metals when grown on acid soils as opposed to neutral or alkaline soils (Sposito and Page 1984).

However, although pH is an important soil variable, it should not obscure the importance of other soil variables such as CEC, clay content, organic matter, or iron oxides. Often the inclusion of two or more such soil variables are employed as independent variables in a multiple regression model to predict the heavy metal concentration in plants among diverse soils (e.g. for cadmium: John *et al.* 1972b, Kuo 1990a, King 1988b, McBride *et al.* 1981). Two important soil criteria which offer a means of controlling the movement in soils and plant uptake of heavy metals in agricultural practices are (see Allaway 1968, Jarvis 1977):

(a) The capacity of the soil to retain metals in a largely unavailable form (Soil Selection).
(b) The maintenance of pH at 6.5 or above by liming, adequate drainage and general soil conditions (Soil Maintenance).

## 5.2.2. Plant Factors Affecting Metal Availability to Plants

There are considerable differences in the ability of plant species to take up individual heavy metals (Jarvis 1977). The evolution of metal tolerance is believed to be quite rapid in both microorganisms and higher plants and is considered to have a genetic basis (Kabata-Pendias and Pendias 1984). Highly specific and multiple metal tolerance may appear within plant species so that ecotypes or varieties of the species have to be taken into account (John and Van Laerhoven 1976). For example, members of the Gramineae family have been shown to have tolerance to metals such as Cd, Pb and Zn (Bradshaw 1952, Simon 1977, Wilkins 1957). The species *Holcus lanatus* has been shown to have metal tolerant populations (Coughtrey and Martin 1977, 1978a, 1978b). Interspecific as well as intraspecific differences therefore exist, e.g. the uptake of Cd (Bingham *et al.*1975, Jarvis *et al.*1976, John *et al.* 1972, Page *et al.*1972).

Uptake into the aerial parts of plants is further complicated by the plant roots. Not only do plants have their own specific forms of root systems but they also have the ability to create their own specific rhizospheric environment, e.g. production of chelating agents and alteration of pH (Brown and Ambler 1973, Elgawhary *et al.*1970, Smiley 1974). Plant roots often function as detoxicating agents by immobilizing and holding back elements that will be toxic to the above-ground structures. The roots themselves can act as an efficient restriction, or barrier, to the movement from roots to shoots of metals such as Cd and Pb taken up from the soil solution (Jarvis 1977, Jarvis *et al.*1976, Jones *et al.*1973). This factor is particularly important in relation to Pb, where most Pb taken up by plants accumulates in the root systems with appreciable amounts only reaching leaves at high soil Pb levels (Davies 1980, Purves 1977). Other factors such as root growth constants, average root radius and water influx rate can all influence plant uptake of metals such as Cd and Zn (Mullins *et al.* 1986). The water influx and transpiration rate will also be affected by the aerial parts of the plant.

Metal uptake can depend on the stage of development of the plant and metal levels will vary between different components of the plant (Chang *et al.* 1984, John *et al.*1972a, Lepp and Dickinson 1987, Matthews and Thornton 1982, Merry *et al.*1985, Mitchell and Burridge 1979, Mitreva 1989, Pepper *et al.*1983, Strickland *et al.*1979). Seasonal influences should also be considered as well as temperature and light (Eriksson 1989, Mattigod and Page 1983, Mitchell and Reith 1966, Thornton 1983). An example of seasonal variation of the distribution of Cu in the different parts of the cultivated oat as the plant

develops is illustrated in Fig.5.2.2 (after West 1981). Examples of metal contents within different components of the plant-soil system and between different species growing upon the same sward are shown in Fig.5.2.3. from Thronton (1983) for the pollutant Cd. A relatively common phenomenon is the accumulation and immobilization of trace metals in roots, especially when their metal supply is sufficient (Kabata-Pendias and Pendias 1984) and/or the metal is non-essential to plant growth (West 1981). This is illustrated in Fig.5.2.3.

## 5.2.3. Heavy Metals and their Availability to Plants.

The ability of different plants to absorb heavy metals and trace elements varies greatly. However, when broadly compared, the index of their accumulating ability illustrates that cadmium, in particular, is very easily taken up (Fig.5.2.4). Due to the "genetic" variability of plants and soils, the trend in Fig.5.2.4 will vary for different soil-plant systems. In most cases, soils with high contents of trace elements support growing plants which also have elevated levels of trace elements in their tissues (Davies 1980, Davies and White 1981). The availability of trace elements to plants is governed by their total concentration in the soil and by the form in which they occur; to a lesser or greater degree depending upon the ambient soil conditions (Thornton and Webb 1980). For example, the contents of Cu, Pb and Zn in pasture herbage from several parts of Wales were higher from soils that had been contaminated by mine waste (Alloway and Davies 1971). However, high concentrations of trace metals found in agricultural soils due to contamination from mining or other anthropogenic sources are usually only reflected in the herbage to a smaller comparative degree (Thornton 1983), such that in some instances, the difference in content of metals in herbage from contaminated and non-contaminated sites may be relatively minimal (Thornton 1980).

### Lead and Copper

Heavy metals such as Pb and Cu are either present in forms relatively unavailable for plant uptake by pasture species or else their uptake and/or translocation are limited by regulatory processes within the plant (Thornton 1979). Indeed, most authors agree that the availability of soil Pb to plants is low and that relatively large differences in soil contents result in only small increases in plant contents (Davies 1980). Herbage Pb contents can remain

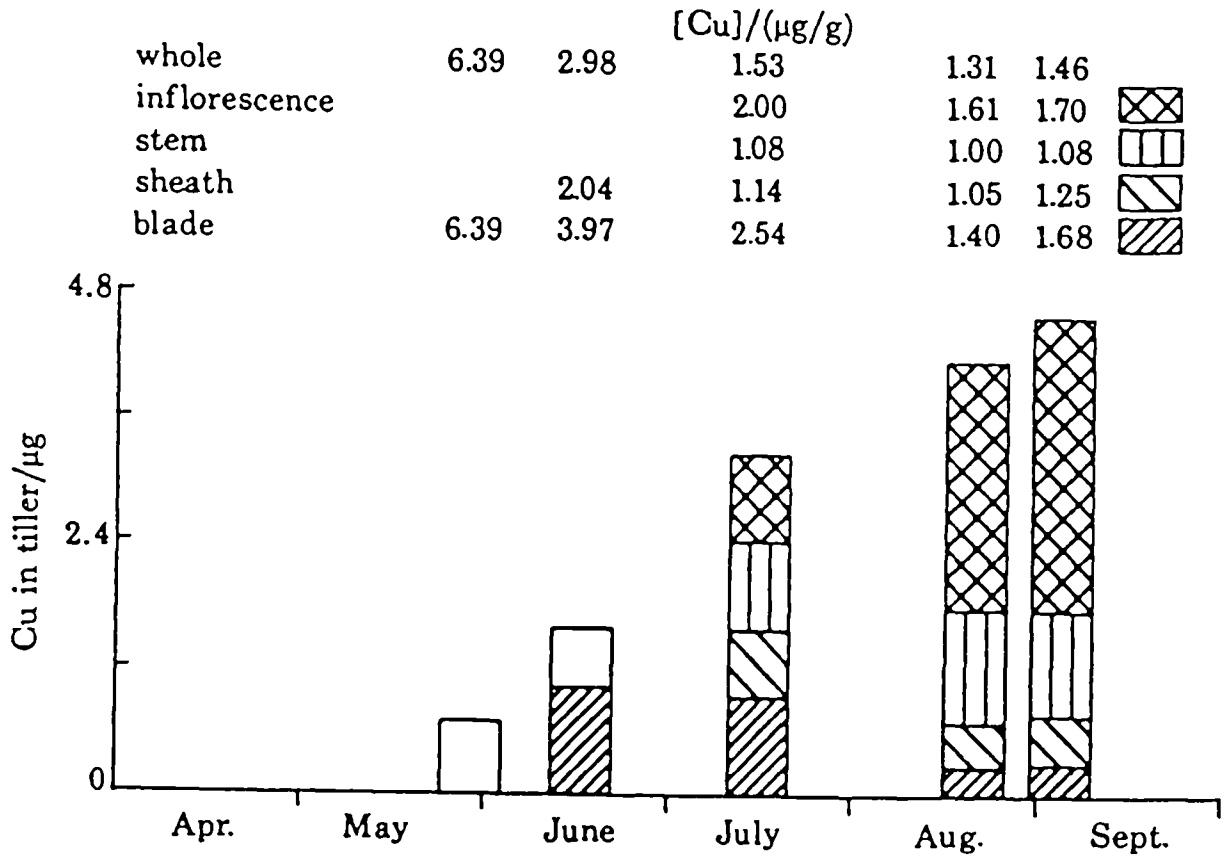


Fig.5.2.2 Seasonal variations in the distribution of copper in the different parts of the cultivated oat, *Avena sativa*, grown on a soil derived from granite.

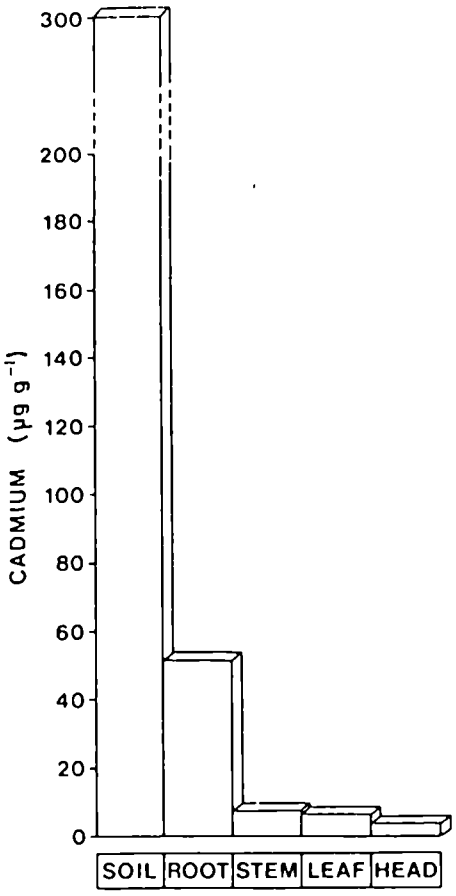


Fig.5.2.3a An example of the cadmium content of soil and the root, stem, leaf and seed head of *Holcus lanatus* at Shipham, Somerset, an area heavily contaminated by past Zn mining (from Matthews and Thornton, 1982).

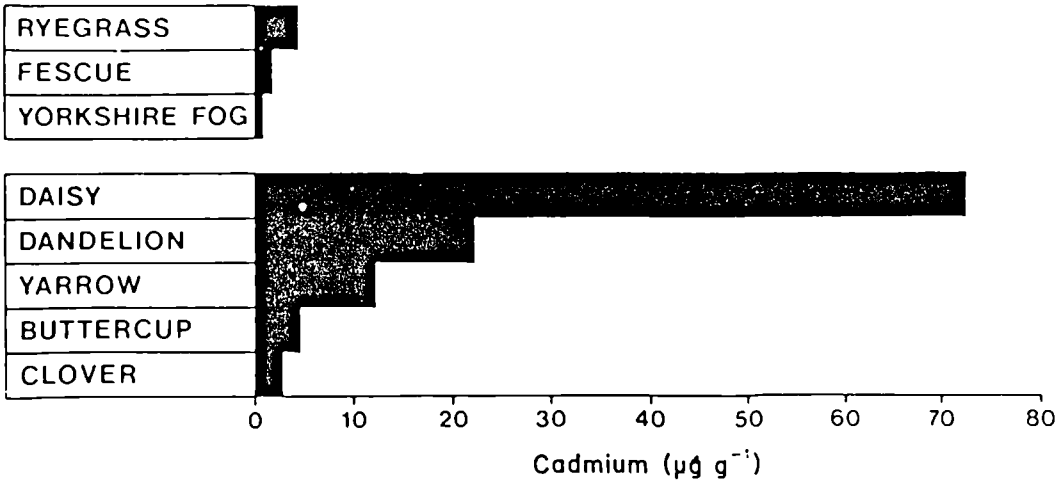


Fig.5.2.3b Variations in the cadmium contents of the aerial parts of common pasture species growing in a contaminated soil at Shipham, Somerset.

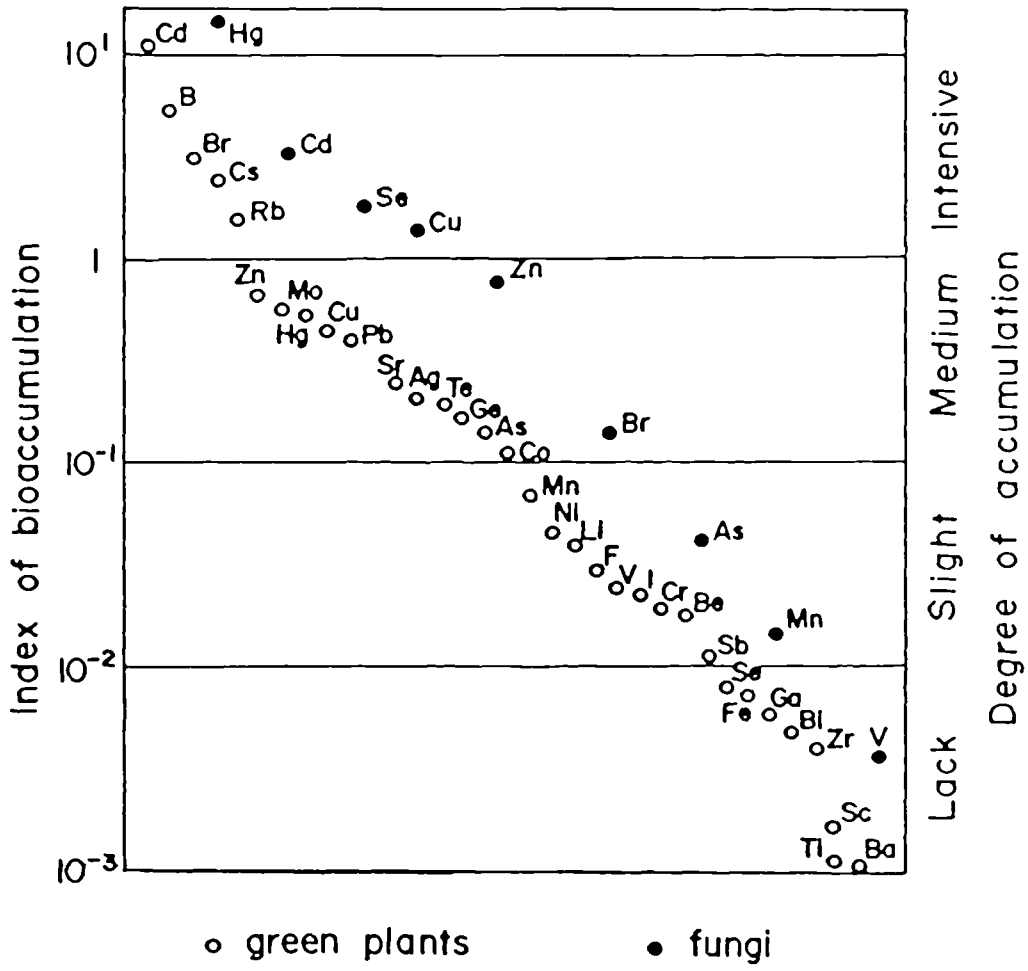


Fig.5.2.4 Bioaccumulation of trace elements by plants from soils. Index of accumulation was calculated as the ratio of trace elements in plants to their concentration in soils. The calculation is based on data for different plants and soils. Values for fungi are based on data from Byrne and Ravnik.

low irrespective of the soil content (Thornton and Webb 1979). Hence, Pb in soil does not often appear to be phytotoxic (MacNicol and Beckett 1985) even at levels in the soil characteristic of heavy contamination (Purves 1977). In comparison to Cd, the phytotoxicity of Pb is relatively low: the binding of Pb to root surfaces and cell walls limits Pb translocation to aerial shoots (Balsberg 1989, West 1981).

Cu tends to be "reluctantly" taken up by plants from soils where the available level is enhanced, so that it is possible for soils to be contaminated with this element to a marked extent without the appearance of any deleterious effects on plants (Purves 1977). Very high concentrations of Cu are required in the growth medium before the root cells become saturated and lose their ability to regulate further transport of Cu to the shoots (Balsberg 1989). Cu is an essential plant element, and plant root tissues have the strong capability of retaining Cu, preventing it's transport to shoots under conditions of both Cu deficiency and Cu excess (Jarvis 1978, 1980, Kabata-Pendias and Pendias 1984). Addition of inorganic and organic forms of Cu to soils quite often has a minimal affect on the concentrations of Cu in pasture herbage, oat, barley and corn where Cu levels in all plant tissue remain within normal ranges (Kornegay *et al.*1976, Mitchell *et al.*1956, Mullins *et al.*1982a, 1982b, Payne *et al.*1988, Thornton 1980, West 1981). Legumes usually have significantly higher concentrations of a number of metals in their shoots than do grasses growing on the same soil (Jarvis 1977). Consequently, clover, which can contain larger amounts of Cu than grasses (Thornton and Webb 1980), can have the ability to show a marked increase in copper content following the addition of Cu to the soil (Mitchell *et al.*1956). However, in general, plants have the ability to restrict their uptake of Cu and Pb.

## Zinc and Cadmium

With luxury levels of soil Zn, this element may be translocated from the roots and accumulated by the tops of the plant: soluble forms of Zn being readily available to plants and the uptake of Zn being reported to be linear with concentration in nutrient solutions and in soils (Kabata-Pendias and Pendias 1984). Indeed, Zn is evidently readily taken up by plants where the available level in the soil is enhanced (Purves 1977). In relation to a metal such as Cu, Zn is seen as "responsive" to changes in soil factors such as pH and total soil metal content (Jeffrey and Uren 1983), and any increase of acidification in Zn-enriched soils may produce more plant available Zn (Balsberg 1989).

One of the major soil factors controlling Zn availability to plants is the pH (Haan and Zwermann 1976). The importance of pH as an independent variable in plant Zn uptake / availability studies has been reported by numerous authors (Davies *et al.* 1987, Haq and Miller 1972, Iyengar *et al.* 1981, Junus and Cox 1987, Kuo *et al.* 1985, Lins and Cox 1988, Martin and Mutters 1985, Pepper *et al.* 1983, Sims 1986, White *et al.* 1979a, 1979b). Likewise, increases in soil and soil solution Zn content can increase uptake and tissue concentrations in plants (Chang *et al.* 1984, Mullins *et al.* 1982a, 1986, Pepper *et al.* 1983) from both inorganic and sludge applications. Hence, Zn phytotoxicity is reported relatively often, especially for acid and heavily sludged soils (Kabata-Pendias and Pendias 1984). Roots often contain much more Zn than do tops, particularly if the plants are grown in Zn-rich soils. Zn, like Cd, is readily taken up by plants and it is therefore expected that it would be involved in most of the short term problems which result from soil contamination (Purves 1977).

Cd, however, in relation to other heavy metals, can be highly toxic to plants and animals at relatively low concentrations (Bingham *et al.* 1979). Cd is highly labile in the soil-plant system: its relative availability to plants being much greater than other potentially harmful heavy metal contaminants such as Pb (Alloway *et al.* 1990). As with Zn, Cd is readily taken up by crops from soil in which it's content has been enhanced (John 1973, Purves 1977). Even at lower soil concentrations (4-13ppm) injury to plants can occur (Bingham *et al.* 1975). Any enhancement of soil Cd levels above the low background level naturally present in topsoil (*È* 0.13ppm acetic acid-extractable Cd) is highly undesirable (Purves 1977).

Many authors have emphasized the importance of soil pH as a factor regulating the solubility of Cd and it's rate of uptake by plants (Eriksson 1989, Kabata-Pendias and Pendias 1984). These include Andersson and Nilsson 1974, John 1972, 1976, John and Van Laerhoven 1976 b, John *et al.* 1972 b, c, Kuo *et al.* 1985, Mahler *et al.* 1978, 1980, Street *et al.* 1978, White and Chaney 1980, Williams and David 1976. With reference to the work by Bingham *et al.* (1975) and Mahler *et al.* (1978, 1980), a model was developed by Browne *et al.* (1984) based upon soil parameters to describe Cd uptake for a number of plant species, where:

$$\log P = a + B \log Cd_{DTPA}$$

and P is plant Cd (μg Cd/g dry weight), $Cd_{DTPA}$ is a measure of available Cd (μg Cd/g soil) and *a* and *B* are linear regression coefficients. *B* was found to be principally a function of soil pH and CEC and *a* was mainly a function of the plant species.

## Influence of Soil Acidification

Increasing acidity of soils liberates bound pools of heavy metals in soils, which may lead to increased availability and uptake of metal ions in plants (Balsberg 1989). Subsequent changes in the metal uptake by roots may have significant nutritional and toxicological consequences to forest trees (Bergkvist *et al.* 1989). Heavy metals such as Cd and Zn appear to be susceptible to soil acidification and their concentrations in solution respond to changes in solution pH (Bergkvist 1987, Bergkvist *et al.* 1989, Tyler *et al.* 1987). There are indications that root uptake of certain metals is increased by soil acidification (Bergkvist *et al.* 1989), and Zn and Cd concentrations in *Anemone nemorosa* have been found to be positively correlated with soil acidity (Tyler 1976).

Hence, within aerially contaminated soils, such as Hallen and Haw Wood, those forms of metals which are most mobile in soil are also likely to be the most bioavailable (Martin and Coughtrey 1987). Obviously, there could be significant consequences for plant / soil health from the mobilization of Cd and Zn (see Chapter 3, Section 4.6.) into the soil rooting zone in heavily aerially contaminated woodland sites that are subject to soil acidification. This is of particular significance as Zn and Cd are more easily translocated within plants than are Cu and Pb; these latter metals being accumulated in roots and the contents in leaves remaining at a normal level until the roots are saturated (Balsberg 1989). Therefore, if mobilization of Pb and Cu into the soil profiles of Haw and Hallen is relatively limited in contrast to Cd and Zn (see Chapter 2, Section 3) then it might be expected that the plant uptake of Cu and Pb would be subdued in relation to uptake of Cd and Zn with respect to the prevailing plant-soil system conditions.

## General: Metal Removal from Soil by Plants and Metal Cycling

Sposito and Page (1984) have presented data for crop removal of different metals from soil:

Rates of metal removal from soil by harvested crops and time required for complete depletion of metal from soil by crops (rate = g/ha/yr, time = 1000's of yrs).

| | Potatoes depletion | | Tomatoes depletion | | Spinach depletion | | Wheat depletion | |
|---|---|---|---|---|---|---|---|---|
| Metal | Rate | Time | Rate | Time | Rate | Time | Rate | Time |
| Cd | 0.79 | 2.0 | 0.22 | 7.2 | 0.57 | 2.8 | 0.06 | 26 |
| Cu | 25 | 5.4 | 6.6 | 20.5 | 6.0 | 22.5 | 8.9 | 15 |
| Pb | 0.14 | 482 | 0.2 | 338 | 0.36 | 188 | 0.04 | 1688 |
| Zn | 85 | 2.6 | 49 | 4.6 | 31 | 7.3 | 53 | 4.2 |

Variations in soil metal concentrations and differences in dry matter production among crops accounted for any differences in the amounts of metals removed. They suggested that for a metal such as Pb, greater amounts were deposited into the soil from the air than removed from the soil by crops, whereas a metal such as Zn was removed by crops at a rate that exceeded amounts deposited onto soil from air in rural regions. Of the 14 trace metals looked at, Zn, Cd and Cu had the fastest depletion times (along with Hg and Mo). Pb had some of the slowest depletion times. The authors' data for metal cycling are shown below:

Cycling of metals within the soil profile by grassland vegetation.

| | Amount deposited on surface by plant residues | Increased metal concentration in upper 0.05m soil |
|---|---|---|
| Metal | g/ha/yr | % |
| Cd | 0.7 | 0.27 |
| Cu | 20 | 0.089 |
| Pb | 10 | 0.089 |
| Zn | 150 | 0.40 |

They suggested that, except possibly for Cd and Zn (and also Hg and Mo), the cycling of the other 14 trace metals, (eg. Cu and Pb) from subsurface to surface soil by vegetation was of little or no importance.

Since the specific properties of plants are very significant in determining the bioavailability of trace elements such as Cd, Cu, Pb and Zn (and are quite variable with changing soil and plant conditions) then, in order to provide an effective evaluation of the pool of bioavailable elements, techniques based on both soil tests and plant analyses should be used together (Kabata-Pendias and Pendias 1984). The crux of the issue is that when attempting to define extractants for metals in relation to plant uptake, soil analysts are likely to find that different extractants provide different degrees of correlation with plant uptake (Beckett*et al.*1983, Låg and Elsokkary 1978, MacNicol and Beckett 1985) between different soils, plant species and metal elements.

To further emphasise the point (with reference to Table 5.2.1), Davies *et al.*(1987) found that none of the extractants used in Table 5.2.1 predicted Cu uptake satisfactorily, including EDTA, which was surprising since EDTA has proved widely useful in identifying copper responsive soils. Therefore, it is unlikely that there will ever be a chemical extractant that will work equally well over a full range of edaphic conditions with regard to plant uptake of metals (Tyler 1976).

## .5. Heavy Metal Toxicity in Plants

An assessment of toxic concentrations and effects of an element on plants is very complex because it depends on so many factors that it cannot be measured on a linear scale (Kabata-Pendias and Pendias 1984). Martin and Coughtrey (1982) provided a list of factors, modified from Chaney (1973) in the latter's discussion of uptake and toxicity in the particular context of sewage / sludge applications:

1) Amount of metal in soil
2) The metal(s) present
3) The soil pH
4) The soil organic matter content
5) The phosphate content of the soil
6) The CEC of the soil
7) Reversion to unavailable forms
8) The plant species concerned
9) Characteristics of the metal(s)
10) Presence of absence of competing ions
11) Phosphate availability

12) Rooting depth of plant and distribution of metals
13) Plant age and seasonal effects
14) Plant species and variety; plant part
15) Soil moisture, aeration, and temperature.

Factors 1 to 8 were important in the consideration of toxicity and factors 1 to 15 were important as regards the accumulation of metals in plants. In addition to Chaney's considerations, Martin and Coughtrey (1982) have suggested that several of the factors (9 to 15) might also affect plant toxicity.

Some studies on young plants have shown that, though their uptake of metals (such as Zn, Cu, Ni or Cd) and their yields of dry matter, were affected by environmental conditions and nutrient status, the "upper critical levels" of these elements (i.e. the lowest tissue concentration of an element at which its toxic effects reduced the production of dry matter) were remarkably independent of these factors (Beckett and Davis 1977, Davis and Beckett 1978, MacNicol and Beckett 1985). The effect of "upper critical levels" is illustrated in Fig.5.2.5. MacNicol and Beckett (1985) suggested that tissue concentrations of young plants, or of young leaves, of crop plants or species used as test plants offer some promise as simple and approximate indicators of toxic levels of elemental pollution of the soil environment. It was suggested that barley might be a suitable test crop (Beckett and Davis 1977, Davis and Beckett 1978). However, barley test crop can provide only an approximate measure of the hazard of heavy metal pollution to other species due to differences in uptake between species and, indeed, cultivars of the same species (MacNicol and Beckett 1985). Further problems with the idea of "upper critical metal levels" are that:

(a) different organs on a plant often attain different concentrations, which also will be affected by their stage of plant development.
(b) interactions between two or more potentially toxic elements may occur.
(c) an element may reduce dry matter yield by impairing root function or by reducing the translocation of a second element to the above-ground parts of the plants.

The matter is complicated further as different races of a plant species can possess different tolerances towards different metals. Hence, there are various external or internal processes by which a plant can effectively "shut out" or "shut in" toxic elements from the plant system. Some of the internal

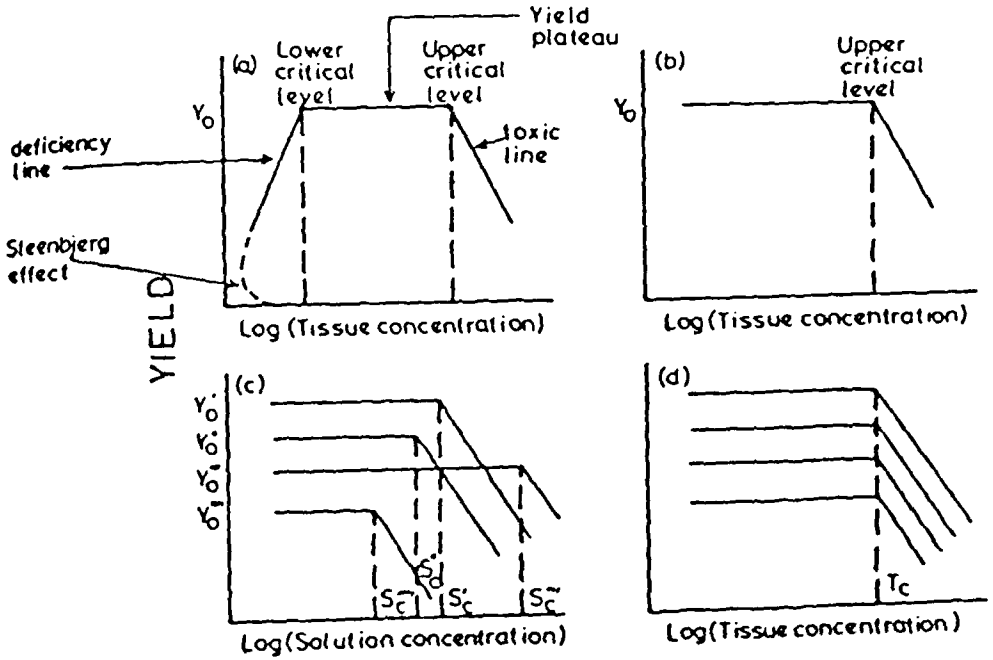


Fig.5.2.5 Diagrammatic yield curves for one crop and one element. (a) and (b) represent single trials with an element that is (a) essential or (b) non-essential. (c) and (d) demonstrate the effect of other factors on the relation between yield and (c) solution or (d) tissue concentrations: $Y_o'-Y_o''''$ are the yields unaffected by toxicity: $S_c'-S_c''''$ are critical solution concentrations: Tc is the critical tissue concentration.

metabolic processes by which a plant can control metal uptake are (Kabata-Pendias and Pendias 1984):

(a) Selective uptake of ions.
(b) Decreased permeability of membranes or other differences in the structure and function of membranes.
(c) Immobilization of ions in roots, foliage and seeds.
(d) Removal of ions from metabolism by deposition (storage) in fixed and/or insoluble forms in various organs or organelles.
(e) Alteration in metabolic patterns - increased enzyme system that is inhibited, or increased antagonistic metabolite, or reduced metabolic pathway by passing an inhibited site.
(f) Adaptation to toxic metal replacement of a physiological metal in an enzyme.
(g) Release of ions from plants by leaching from foliage, guttation, leaf shedding, and excretion from roots.

Some species of plant have the ability to accumulate >10% (ash weight basis) of a heavy metal within their tissues. For example, *Alyssum bertolonii* accumulates Ni, while *Thlaspi calaminare* accumulates Zn; and other species have also been reported to accumulate metals (e.g. Reeves and Baker 1984, Baker *et al.*1985). Another factor to take into account is that some tolerant ecotypes may be stimulated in their growth by the presence of higher amounts of metal within the plant-soil system (Antonovics *et al.*1971, Cox and Hutchinson 1980).

Nevertheless, despite the variability in plants to uptake and withstand metals within the plant system, some attempts have been made to provide data on deficient, normal and or excessive / toxic levels of metals in plants (in most cases from an extensive body of literature). Tables 5.2.2-5.2.5 provide a fair idea of the important concentration ranges to be found in plants.

MacNicol and Beckett (1985) suggested that if the tissue concentration of any crop, and particularly of a barley test crop, on a site suspected of elemental pollution, measured below any of 5mg/kg Cd, 10 mg/kg Cu or 100 mg/kg Zn then it was not these elements that were causing a reduction in yield. Balsberg (1989) suggested that, although there was great variation between plant species, critical leaf tissue concentrations affecting growth in most species was in the order of 200-300ug/g Zn, 15-20ug/g Cu and 8-12 ug/g Cd (all on a dry weight basis).

Table 5.2.2 General concentration ranges of Cd, Cu, Pb and Zn (mg/kg dry wt.) found in land plants, vegetables and grasses. 1 = from Bowen (1979), 2 = from Kabata-Pendias and Pendias 1984, 3 = Allaway (1968).

| Element | Landplants[1] | Vegetables[1] | Grasses[2] | Landplants[3] |
|---|---|---|---|---|
| Cd | 0.1 - 2.4 | 0.05 - 0.9 | 0.03 - 1.26 | 0.2 - 0.8 |
| Cu | 5 - 15 | 4 - 20 | 1.1 - 33.1 | 4 - 15 |
| Pb | 1 - 13 | 0.2 - 20 | 0.19 - 9.0 | 0.1 - 10 |
| Zn | 20 - 400 | 1 - 160 | 6 - 80 | 15 - 200 |

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Table 5.2.3 Approximate concentrations of Cd, Cu, Pb and Zn in mature leaf tissue generalised for various species (mg/kg dry wt.) from Kabata-Pendias and Pendias (1984). N.A.=not applicable.

| Element | Deficiency | Sufficient or Normal | Excessive or Toxic |
|---|---|---|---|
| Cd | N.A. | 0.05 - 0.2 | 5 - 30 |
| Cu | 2 - 5 | 5 - 30 | 20 - 100 |
| Pb | N.A. | 5 - 10 | 30 - 300 |
| Zn | 10 - 20 | 27 - 150 | 100 - 400 |

---

Table 5.2.4 Critical levels of Cd, Cu, Pb and Zn in young Spring barley (from Davis *et al* 1978) and in solution culture media.

| Element | In Tissue (µg/g dry wt.) | In Solution (µg/ml) |
|---|---|---|
| Cd | 14 - 16 | 0.5 as $Cd^{2+}$ |
| Cu | 18 - 21 | 4 as $Cu^{2+}$ |
| Pb | 20 - 35 | 25 as $Pb^{2+}$ |
| Zn | 160 - 320 | 9 as $Zn^{2+}$ |

**Table 5.2.5 Summary of advisory experience in England and Wales on Cu and Zn levels (mg/kg dry wt.) in soils and plants (from Williams 1975 in MacNicol and Beckett 1985).**

| Element | Extractant | Normal Range Soil | Toxic Range Soil |
|---|---|---|---|
| Cu | 0.05M EDTA | 0.5 - 5 | 50 - 100 |
| Zn | 0.5M HOAc | 1 - 50 | 100 - 200 |

| | Normal range Plants | Toxic Range Plants |
|---|---|---|
| Cu | 5 - 15 | >25 |
| Zn | 20 - 200 | >200 |

---

There is some consensus of opinion that suggests that Cd is the most phytotoxic element of the four metals (Cd, Cu, Pb and Zn), whereas Zn is the least phytotoxic (e.g. see Balsberg 1989). In terms of sludge-amended soils (Chumbley 1971, Patterson 1971, Webber 1972 - see Bingham *et al.* 1979) the "zinc equivalent" suggests that Cu is twice as phytotoxic as Zn. In terms of excessive toxic concentrations in plants, Tables 5.2.3 and 5.2.4 suggest that the order of phytotoxicity is Cd > Cu > Pb > Zn.

## 5.2.6. Metal Interactions and Plant Availability

Interactions between Zn, Cu, Cd, Pb and other metals (and indeed non-metals) within the soil and within the plant provides another grey area of unpredictability when assessing availability of an element for uptake by a plant. The various forms of interactions that can occur between two elements (A and B) are given in Fig.5.2.6 from MacNicol and Beckett (1985).

Results from interactive studies illustrate that the subject is far from clear cut for a metal-metal interaction. For example, Zn-Cd interactions have been studied: antagomism and synergism have all been reported (e.g. Bingham *et al.* 1979, Haghiri 1974, John 1976, Jones *et al.* 1976, Lagerwerff and Biersdorff 1972, Maclean 1976, Singh and Steinnes 1976, Wallace *et al.* 1980). Hughes *et al.* (1980) tabulate numerous references involving interactive effects on heavy metal uptake in plants, and further coverage is also given by Kabata-Pendias and Pendias (1984).

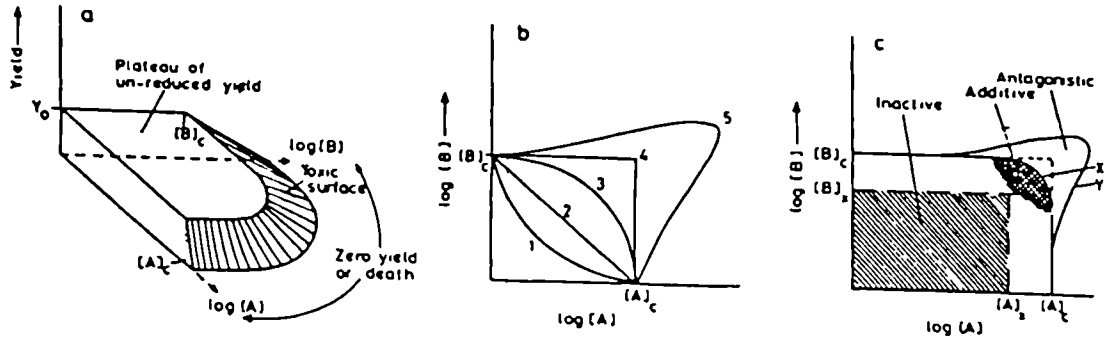


Fig.5.2.6 The combined toxic effects of two elements (A and B) shown diagrammatically.

a) Yield as a function of Log [A] and Log [B], where [A] and [B] are tissue concentrations. The left and back faces correspond to the yield curves of A and B alone : $[A]_c$ and $[B]_c$ are their upper critical levels: the *yield plateau* comprises all non-toxic combinations of A and B; the *toxic surface* comprises all toxic non-lethal combinations of A and B: the *scarp* between them represents the limit of non-toxic combinations.

b) Various forms of interactions between A and B:

(1) *Synergistic* – the toxic effects of one or both elements increased by the presence of the other;

(2) *Additive* – toxicity in proportion to Log [A] + Log [B] (≡ Log AB);

(3) *Additive* – toxicity in proportion to Log [A + B];

(4) *Independent* – neither element has any toxic effects below its critical level, regardless of the concentration of the other;

(5) *Antagonistic* – it requires more of one element to produce toxicity in the presence of the other than in its absence.

c) The forms of the interactions between Cu/Zn, Cu/Ni, Zn/Ni in young barley lay between x and y. Except in their middle regions the scarps lay perpendicular to the critical levels on both axes. It would seem that, whether their interactions were additive (3), independent (4) or antagonistic (5), it was only those increments of A and B above the threshold concentrations $[A]_x$ and $[B]_x$ that interacted.

The major problem within a soil-plant system is that it is a multielemental-nutrient system and hence the interactive combinations that could take place are large. Also, metal uptake and toxicity are closely related and toxicity to one metal may affect the uptake and toxicity of another metal (Martin and Coughtrey 1982). In the case of the Zn-Cd interaction a factor such as the ratio of Cd to Zn in the plant media might control the occurrence of synergism and antagonism between these metals (Kabata-Pendias and Pendias 1984).

## 5.2.7. Concluding Remarks

Assessment of the plant availability of heavy metals such as Cd, Cu, Pb and Zn in soils is fraught with areas of uncertainty. There are numerous factors that can affect uptake of heavy metals in plants and heavy metal tissue concentrations (see Sections 5.2.1-5.2.6). Thornton (1983) suggested that the concentrations of trace elements in plant tissues were governed by their total concentration in the soil, the forms in which they occurred and by some soil and plant factors influencing their mobilization in soils, availability and uptake by plants and the subsequent translocation within the plants. This last statement serves to illustrate that there is no succinct way in which the uptake of metals such as Cd, Cu, Pb and Zn can be adequately described.

Thus, it is perhaps expecting too much for a chemical extractant to "reflect" the uptake of an element in a plant as it measures only the extractable element subject to conditions of the soil, the extractant and the behaviour of the element within the soil suspension. Furthermore, much of the emphasis in plant uptake and availability of heavy metals appears to be based on the triad of factors related to the soil, plant and element(s) of concern. One aspect of interest that has not been mentioned as yet is the role of soil microorganisms in plant metal uptake. This "biological" factor is perhaps best encapsulated within the group of "soil" factors that affect uptake, although the effect of a mycorrhizal infection on plant metal uptake could depend as much on the species / variety of the fungus as it would on the plant.

The complexity of "interaction" and "response" points towards the "genetic" basis upon which plants and soils (and indeed the element of interest) are established. Fig.5.2.7 demonstrates how different plant-soil systems respond to changes in soil pH. Not only can the plant tissue concentration vary with pH change and soil type, but also with plant species. The data provide further interest, however, as the corn plants grown on soils 5, 7 and 8 are probably deficient of Zn (see Table 5.2.3). This is ratified by

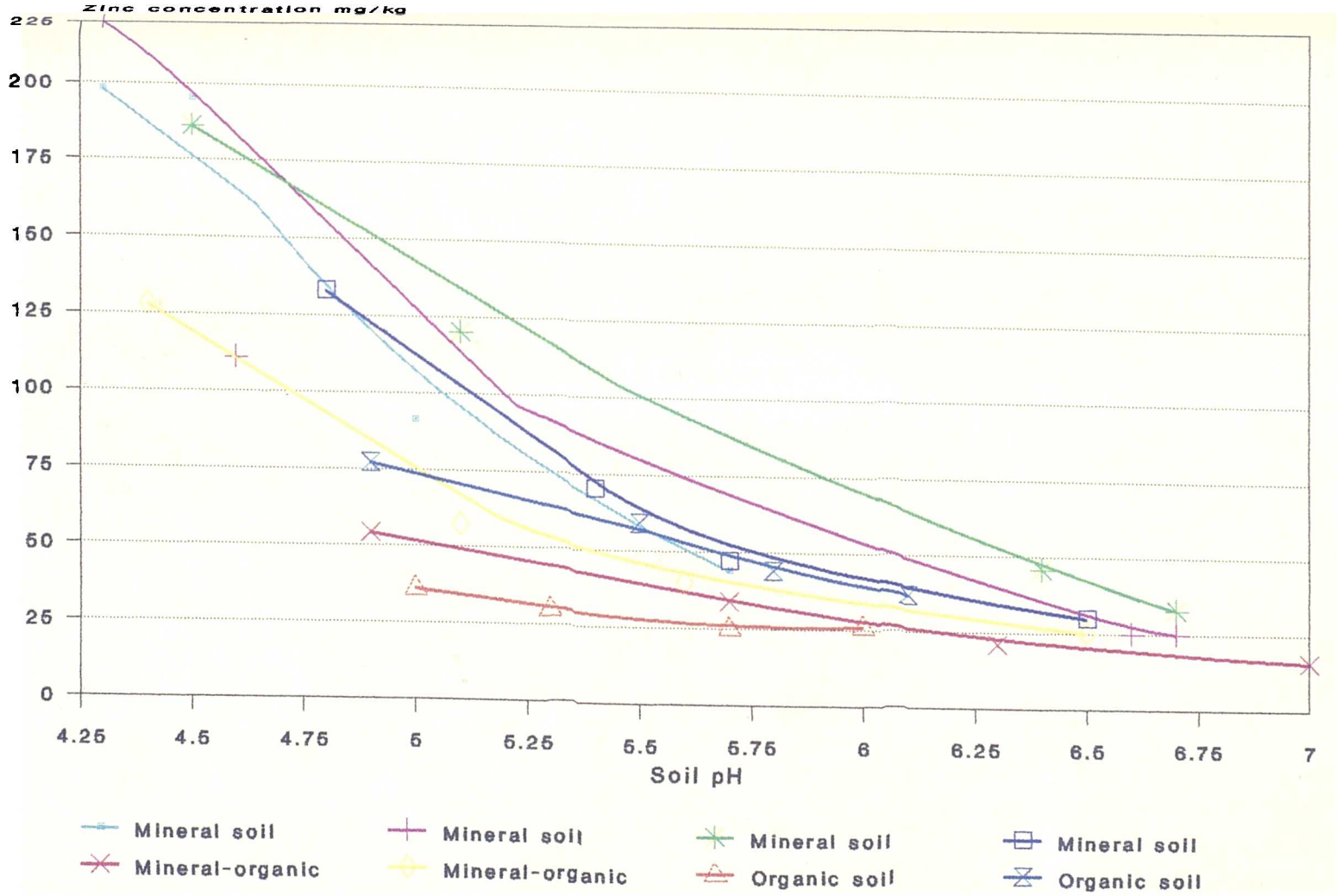


Fig.5.2.7a Effect of Soil pH on Plant Zn after growing Soybeans on 8 Greenhouse Soil Types (data from Junus & Cox 1987)

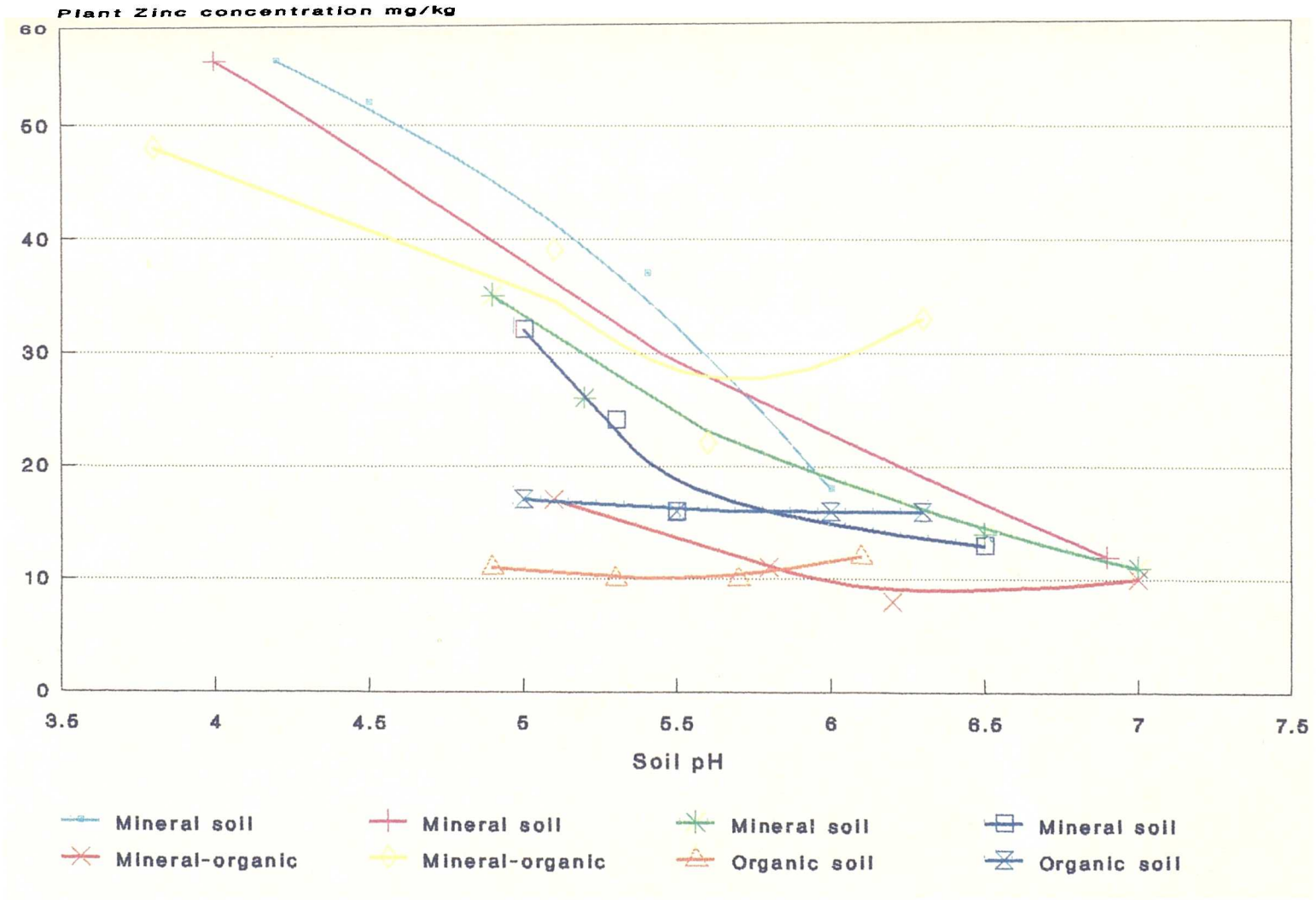


**Fig.5.2.7b Effect of Soil pH on Plant Zn after growing Corn on 8 Greenhouse Soil Types (data from Junus & Cox 1987)**

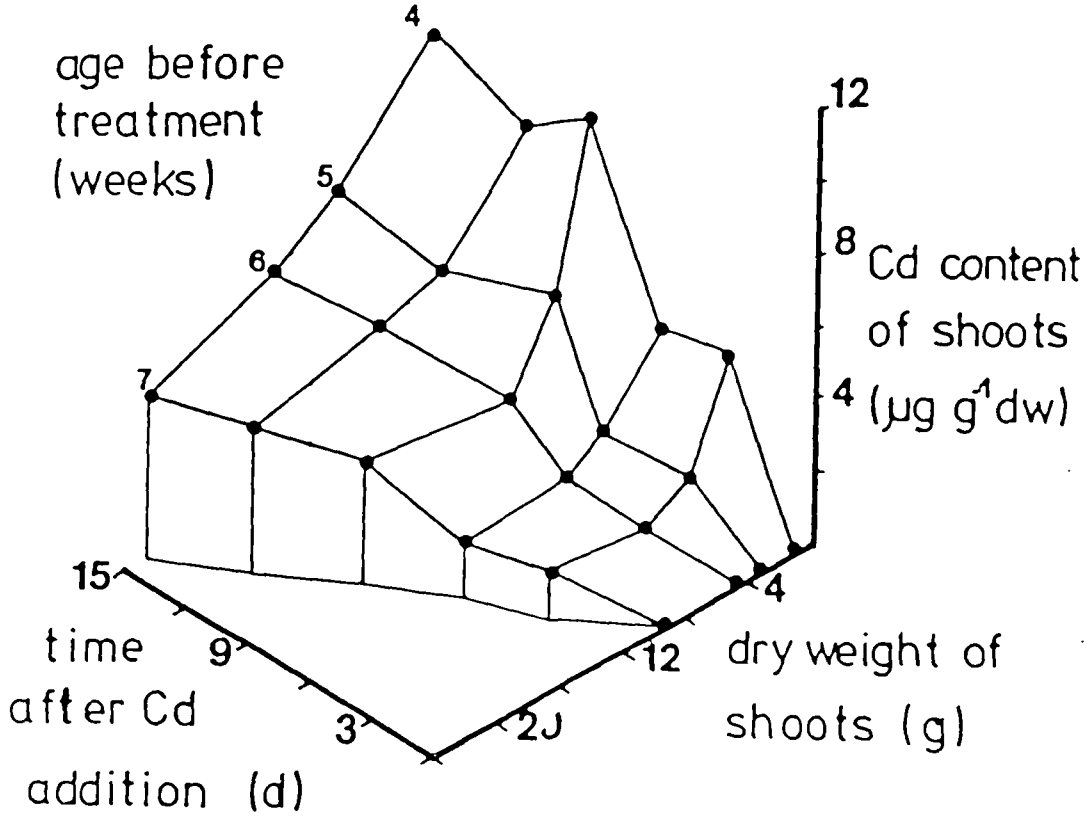


Fig.5.2.8 Relationships between dry weight and cadmium concentration of ryegrass, and also time at application of cadmium in flowing solution culture. (From Jarvis and Jones, 1978.)

Junus and Cox (1987) who make reference to critical plant deficient levels of Cox and Wear (1977) and Melsted *et al.* (1969).

It is therefore also important to consider the general health and state of the plant in its ability to take up the element of interest. Stage of development of the plant and time of sampling the plant material all affect the outcome of the final result (e.g. data from Jarvis and Jones (1978) plotted out by Martin and Coughtrey (1982) in Fig.5.2.8). Fig.5.2.8 serves to emphasize that there is often a wide dimension of factors to be considered in assessing plant metal uptake. In a similar context, soils develop and change with time (Brockheim 1980) and hence a soil that responds and adapts to its environment will influence plant uptake of an element accordingly.

With respect to aerially contaminated woodland sites such as Hallen and Haw Wood, Martin and Coughtrey (1981) picked out four factors which differentiated such sites from other contaminated sites (e.g. mine spoil):

(a) A lesser degree of contamination (although continuous).
(b) A lack of major disruption, at least in the first instance, of soil nutrient conditions.
(c) No physical destruction of the soil aggregates.
(d) The lack of clear-cut boundaries between contaminated and uncontaminated sites.

They suggested that the combination of above factors might operate adaptive mechanisms within plants which differed from those of mining or naturally contaminated sites and thus created other complications in the furtherance of conclusions concerning the long-term ecosystem effects of heavy metals.

With respect to the differential course of evolutionary developments taking place in the heavy metal soil profiles of Hallen and Haw Wood (see Chapter 2, Section 3), there hangs the question of whether these two sites contain plant species (e.g. *Holcus lanatus*) that have adapted differential degrees of metal tolerance despite the geographical proximity of the two sites (see Coughtrey and Martin 1977, 1978a, 1978b). In a similar context, would the multiple tolerance of *Holcus lanatus* (Martin and Coughtrey 1978b) adapt to any significant increases in available toxic elements such as aluminium as acidification of soils in Hallen Wood continues? With the additional impact of aerial deposits and foliar uptake, combined with the changing distribution of metals with time in the soil profiles at Haw and

Hallen Wood, one can imagine that the "genetic plasticity" of some species will be tested to the full resulting in the decline and perhaps loss of some plant species.

## 5.3. Bioassay of Cd, Cu, Pb and Zn in Haw and Hallen Wood Soils.

### 5.3.1. Methodology

In order to gain a biological assessment of the available metal contents of Cd, Cu, Pb and Zn in the Hallen and Haw Wood soil profiles, subsamples of soil from each layer of soil (apart from the L, F, H organic layers) were potted. Ten pot replicates were used for each individual layer (i.e. 0-1cm, 1-3.5cm, 3.5-6.0cm etc. to a depth of 46cm in Haw Wood soil and 61cm in Hallen Wood soil). Crushed air-dried soil (< 2mm in diameter mixed with perlite in a 3:1 soil: perlite mix) was put into 2" pots. Perlite had to be added to the soil in order to give the crushed soil some structure. The nature of the clayey soil material meant that too little water could cause the clay to bake hard and too much water could create waterlogged conditions. The perlite addition helped to ameliorate the physical condition of the soil within the pots. Apart from the "dilution" effect of the perlite, no additions of fertilizer etc. were made so that each pot "reflected" the chemical nature of the soil material used.

The grass *Holcus lanatus L.* (Yorkshire Fog) was used as the test plant. Certain features about the species made it suitable as a test plant (see Grime *et al.*1988):

(a) Recorded, at least as seedlings, in every type of habitat. Greatest abundance in meadows and pastures. However, it also occurs on spoil heaps, waste ground, grass verges, paths, hedgerows and, to a lesser degree, stream banks, arable land, marshy ground, skeletal habitats, scrub and woodland clearings. (Also found in grassy habitats near the sea and on mountains).

(b) It is frequent and abundant at all altitudes (up to 610m), found on a wide range of slopes and aspects.

(c) Although most typical of moist soils, the grass is common in wetland, particularly in soligenous mire. It has also been recorded from temporarily submerged sites (water depth up to 1m).

(d) Most frequent and abundant on soils of intermediate base status (pH5.0-6.0), but relatively common over the pH range 4.5-8.0. Few records from highly acidic soils.
(e) The ordination suggests that is has an extremely wide-ranging distribution.

The grass seeds were collected from a relatively clean site in the Cotswolds. Grass heads were rubbed and chaffed to collect seed, which in turn were grown on watered (deionised) perlite bases. Once the seedlings were over and above 2.5cm in height, they were planted in the prepared pots and allowed to grow for a six week period. Pots were watered with deionised water at the basal dish to avoid soil splash. At the end of the growing period, the plant height was measured. Plants were then harvested, oven dried at 70-80°C and weighed. The material was then digested in concentrated Aristar nitric acid and concentrations were measured by FAAS for Zn and GFAAS for Cd, Cu and Pb (see Appendix A).

## 5.3.2. Results of the Haw and Hallen Wood Bioassay.

Results of the plant tissue concentrations of Cd, Cu, Pb and Zn are given in Fig.5.3.1 for both woodland soils. The Pb concentrations were recorded between 0-8 mg/kg which is within the "normal range" for both plant and grass tissues (see Tables 5.2.2 and 5.2.3). All of the Cu concentrations were 15 mg/kg or less in both soils and mainly ranged between 5-15 mg/kg which is the normal tissue concentration for most plants (see Tables 5.2.2, 5.2.3 and 5.2.5). In some instances, Cu concentrations were low enough to perhaps be classed as "deficient".

At 6-46cm depth in Haw soil and 48.5-61cm in Hallen soil, the Zn concentrations conformed to the "normal range" for Zn in plants (Table 5.2.3 and 5.2.5) and grasses (Table 5.2.2). At 0-6cm depth in Haw Wood, the Zn concentrations could be considered "excessive" (see Tables 5.2.3 and 5.2.5) but were unlikely to be "toxic" (see Tables 5.2.3, 5.2.4 and 5.2.5 - also Balsberg 1989). Similarly, Zn levels in plants at 0-16cm and 31-48.5cm depth in Hallen Wood were also probably excessive. However, between 16-31cm depth in Hallen soil, the Zn levels in the plant tissue were potentially at phytotoxic levels (see Tables 5.2.4, 5.2.5 and Balsberg 1989).

Only at depths > 21cm in Haw Wood and 56cm in Hallen Wood did Cd levels reach the "normal range" of Cd concentrations found in grasses in

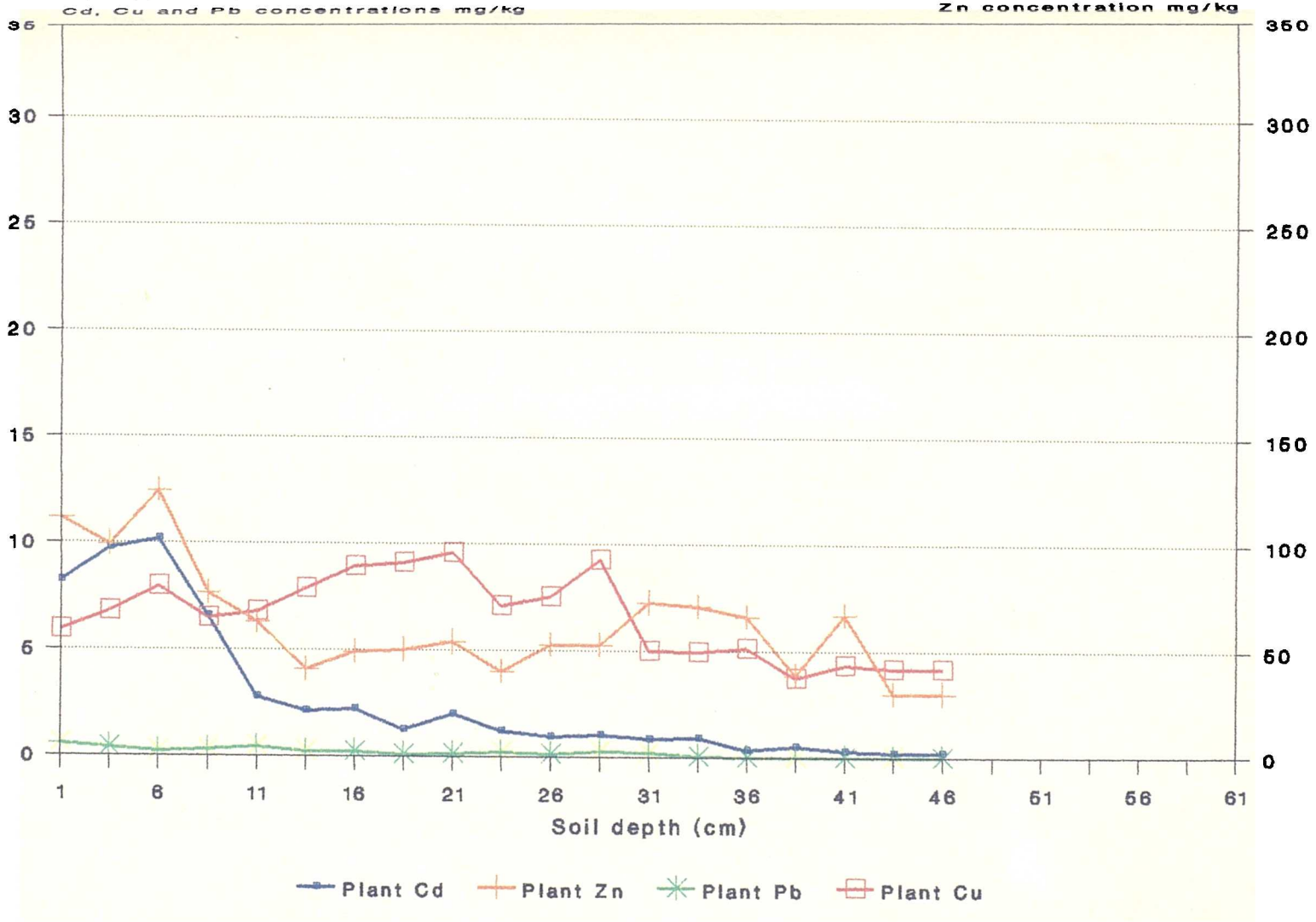


**Fig.5.3.1a Haw Wood Heavy Metals in *Holcus lanatus***

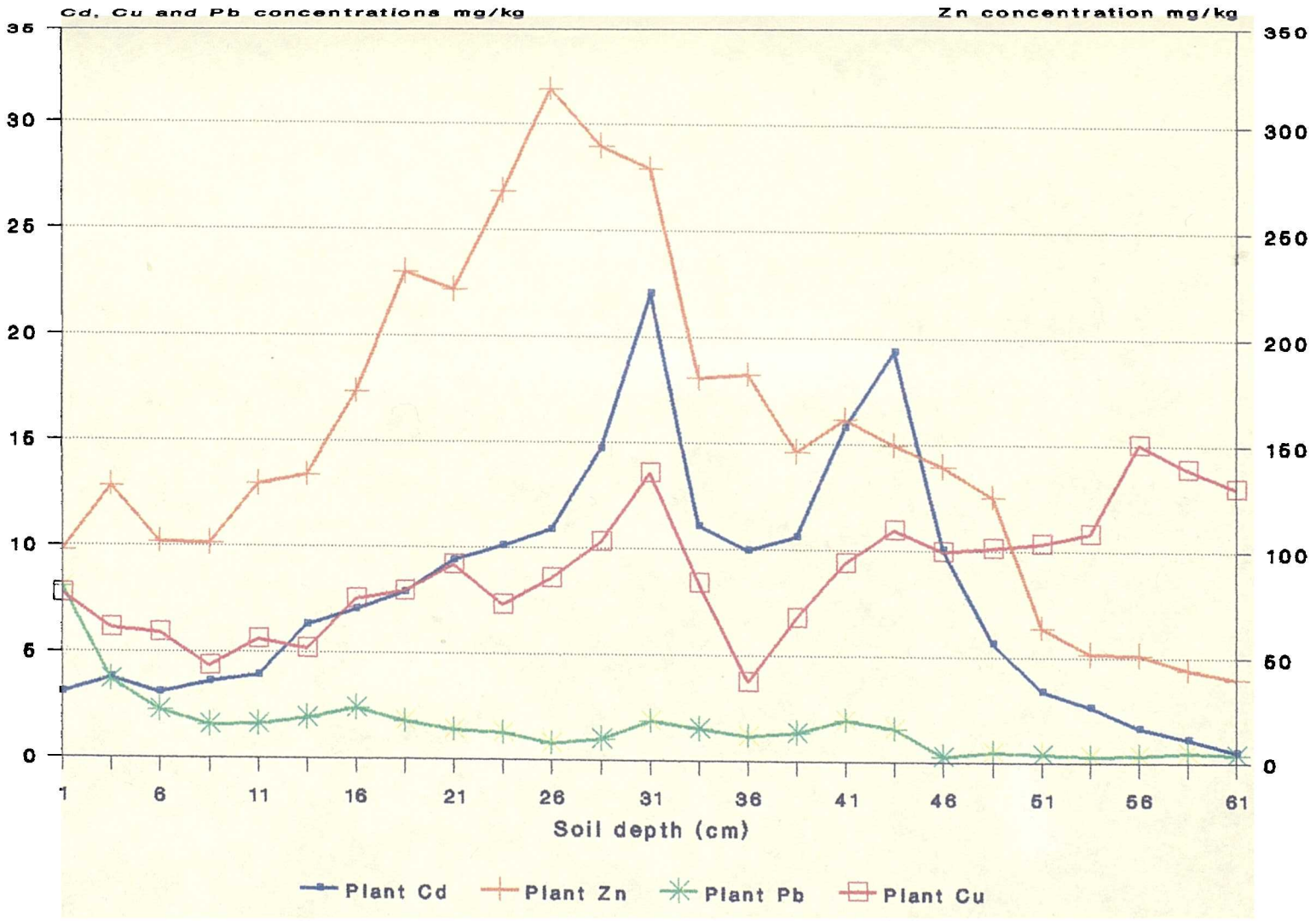


**Fig.5.3.1b Hallen Wood Heavy Metals in *Holcus lanatus***

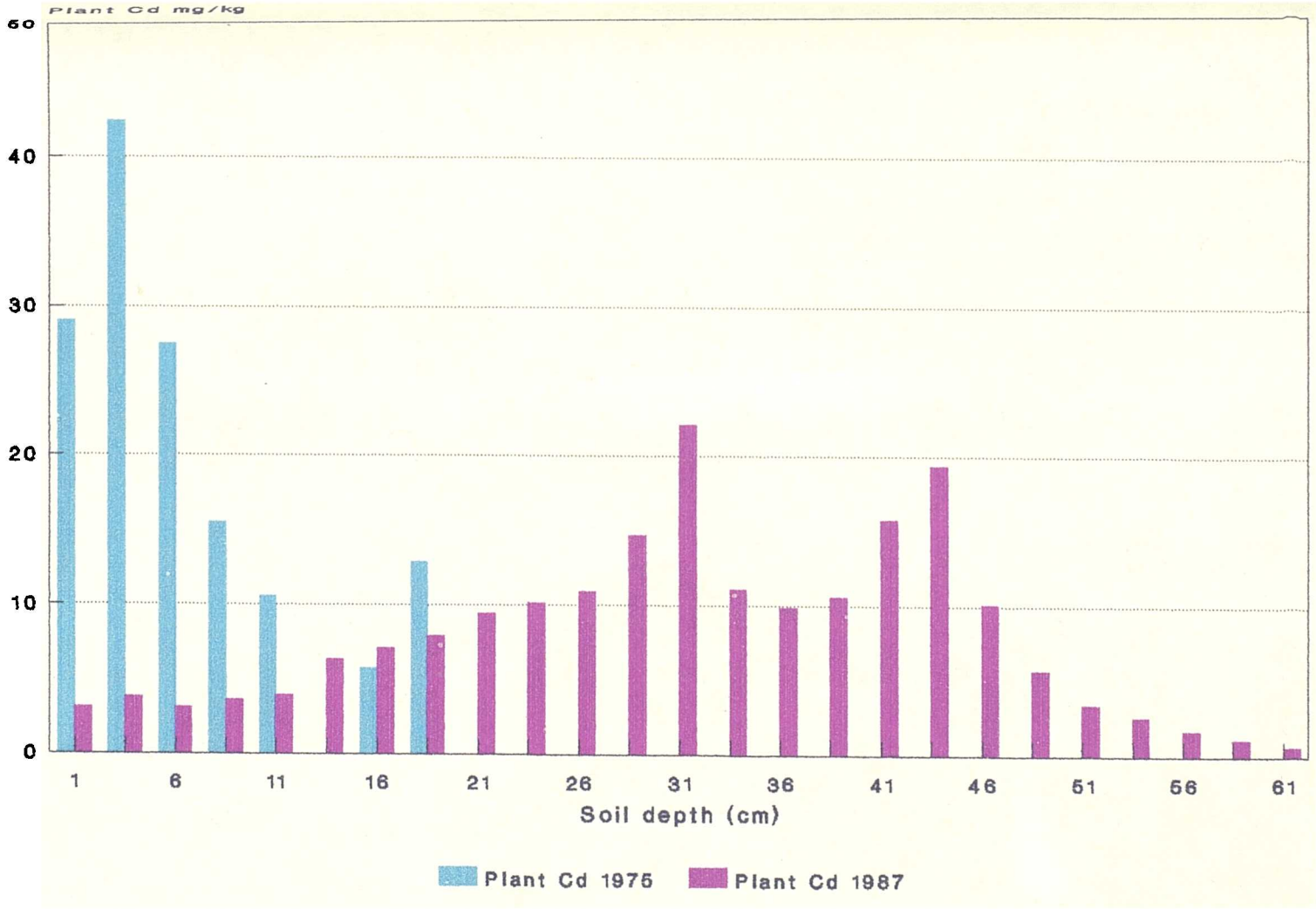


**Fig.5.3.1c Cadmium concentrations in Holcus lanatus grown on Hallen Wood 1975 and 1987 soil profiles.**

Table 5.2.2. If the range of Cd levels in landplants is considered in Table 5.2.2 then *Holcus lanatus* tissue concentrations at depths > 11cm in Haw Wood and > 53.5cm in Hallen Wood were within the normal range. Excess Cd tissue concentrations of 5 mg/kg or larger (see Table 5.2.3) may cause reductions in plant yield (MacNicol and Beckett 1985) and plant tissue concentrations in the range of 8-16 mg/kg (Table 5.2.4, Balsberg 1989) may potentially be phytotoxic to plants. Between 0-6cm depth in Haw and 16-46cm in Hallen, the Cd levels in *Holcus lanatus* were 8 mg/kg or greater and therefore such levels could jeopardize the vitality of the grasses grown at these soil depths. Fig.5.3.1c provides a comparison between Cd concentrations found in *Holcus lanatus* grown on Hallen soils of the mid 1970's (Coughtrey 1978) and the present 1987 profile.

From the data provided for "normal" metal ranges in plants in Tables 5.2.2 and 5.2.3, it might be expected that the general concentration levels of metals in a plant normally follow the order:

$$Zn > Cu \geq Pb > Cd$$

In Haw Wood, the levels of metal tissue concentrations followed the order:

$$Zn > Cu > Cd > Pb$$

The exception to the above order was in the first 8.5cm of soil where the Cu and Cd positions were reversed. In Hallen Wood, metal tissue concentrations to 46cm depth generally followed the order:

$$Zn > Cd \geq > Cu > Pb$$

At depths > 46cm, the above order pertaining to Haw Wood was true for Hallen Wood. In the surface layers of Hallen soil Pb tissue concentrations became more prominent and Cu levels asserted dominance in relation to Cd recorded levels.

The graphs in Fig.5.3.1 have been plotted on the same concentration scales to provide some comparative perspective of the tissue concentrations within the plants. Comparison of the top 46cm of both soils would suggest that the levels of Zn, Cd and Pb were probably greater in the Hallen grown grass. This is confirmed by the t-values presented in Table 5.3.1

**Table 5.3.1 Results of student's t-test : test for differences between plant tissue concentrations of Cd, Cu, Pb and Zn in *Holcus lanatus* grown on Hallen and Haw Wood soils (t-tests for available soil metal also included) to 46cm depth.**

| Metal | Plant Concentration | Exchangeable Fraction in Soil | Sequentially Extractable Fraction in Soil |
|---|---|---|---|
| Cd | $4.73^{***}$ | $12.79^{***}$ | $5.74^{***}$ |
| Cu | 1.76 | $10.32^{***}$ | $8.85^{***}$ |
| Pb | $4.75^{***}$ | $2.07^{*}$ | 1.76 |
| Zn | $7.07^{***}$ | $6.68^{***}$ | $3.18^{**}$ |

*** : $p \leq 0.1\%$ ** : $p \leq 1\%$ * : $p \leq 5\%$ n = 19

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Significant differences between the woodland soils in the amount of "available" Cd and Zn would account for the difference in plant tissue concentrations for these two metals between woodland soils.

Due to the high variance created in the Pb data sets for soil availability (due to high values in the top 8.5cm of soil), the differences in the available Pb content between the two woodland soils is not apparent in Table 5.3.1. To illustrate the point, if the first four data pairs of the Pb sequential extraction dataset were removed, then the t value became 5.21 ($p \leq 0.1\%$) instead of $t = 1.76$ ($t > 5\%$). This indicates that uptake of Pb by *Holcus lanatus* was probably responsive to differences in the available Pb within the two soils below 8.5cm depth; but excessive elevated available Pb levels in the top 0-8.5cm did not produce the same excessive response in the plant Pb concentrations which otherwise would have produced excessive variance.

The Cu t-value results are interesting as the significant differences between woodland soil available levels are not expressed by any significant difference in the Cu plant tissue concentrations. Visual observation of the data on Fig.5.3.1 illustrates that most Cu tissue concentrations from both woodland soils fluctuated between 4-10 mg/kg. Removal of the highest (13.6 mg/kg) or lowest (3.7 mg/kg) values from the Hallen dataset (which lie outside the 4-10 mg/kg range) produced respective t-values of 1.27 and 1.97 which are still less than the 95% confidence level.

In the Hallen profile, *Holcus lanatus* Cd and Zn levels at 51-53.5cm depth and greater were less than any recorded further up the Hallen profile, and were equivalent to those Cd and Zn plant concentrations found at 11-13.5cm or deeper in the Haw Wood profile. At 43.5-46cm depth and greater, Pb plant concentrations grown on Hallen soil attained levels equivalent to those found throughout the Haw profile. Conversely, Cu concentrations in Hallen grown plants maintained their levels of Cu at or above 10 mg/kg at depths >41cm depth, whereas most of the rest of the Hallen grown plants and all the Haw grown plants reached levels <10 mg/kg.

The ratio of plant tissue concentration (mg/kg) to the total soil metal concentration (mg/kg) for the two woodland soils is illustrated in Fig.5.3.2. This ratio provides an approximate assessment of heavy metal plant availability in the soil with respect to the concentrations of metals attained in the aerial parts of the grass tissue. Within the Hallen profile, the availability of the metals in the soil appeared to follow the order of:

$$Cd > Zn \geq Cu > Pb$$

In Haw Wood between 0-21cm depth, the order was:

$$Cd > Cu \geq Zn > Pb$$

and 21-46cm :

$$Cd \geq Zn > Cu > Pb$$

Fig.5.3.3 shows the amount of metal taken into the aerial parts of *Holcus lanatus* in relation to the amount of metal retained in the soil and roots. This takes into account the mass of soil used in each pot and the mass of the aerial parts of *Holcus lanatus* assay plants. In this respect, the health and or productivity of the plants has been acknowledged to some degree :

i.e.

$$\frac{\mu g \text{ metal in plant tissue} \times 100\%}{\mu g \text{ metal in soil}}$$

This should provide some indication of the extraction efficiency of the plants. Fig.5.3.3 demonstrates that the metal availability within the two soils to the grasses closely followed the order outlined above for Fig.5.3.2.

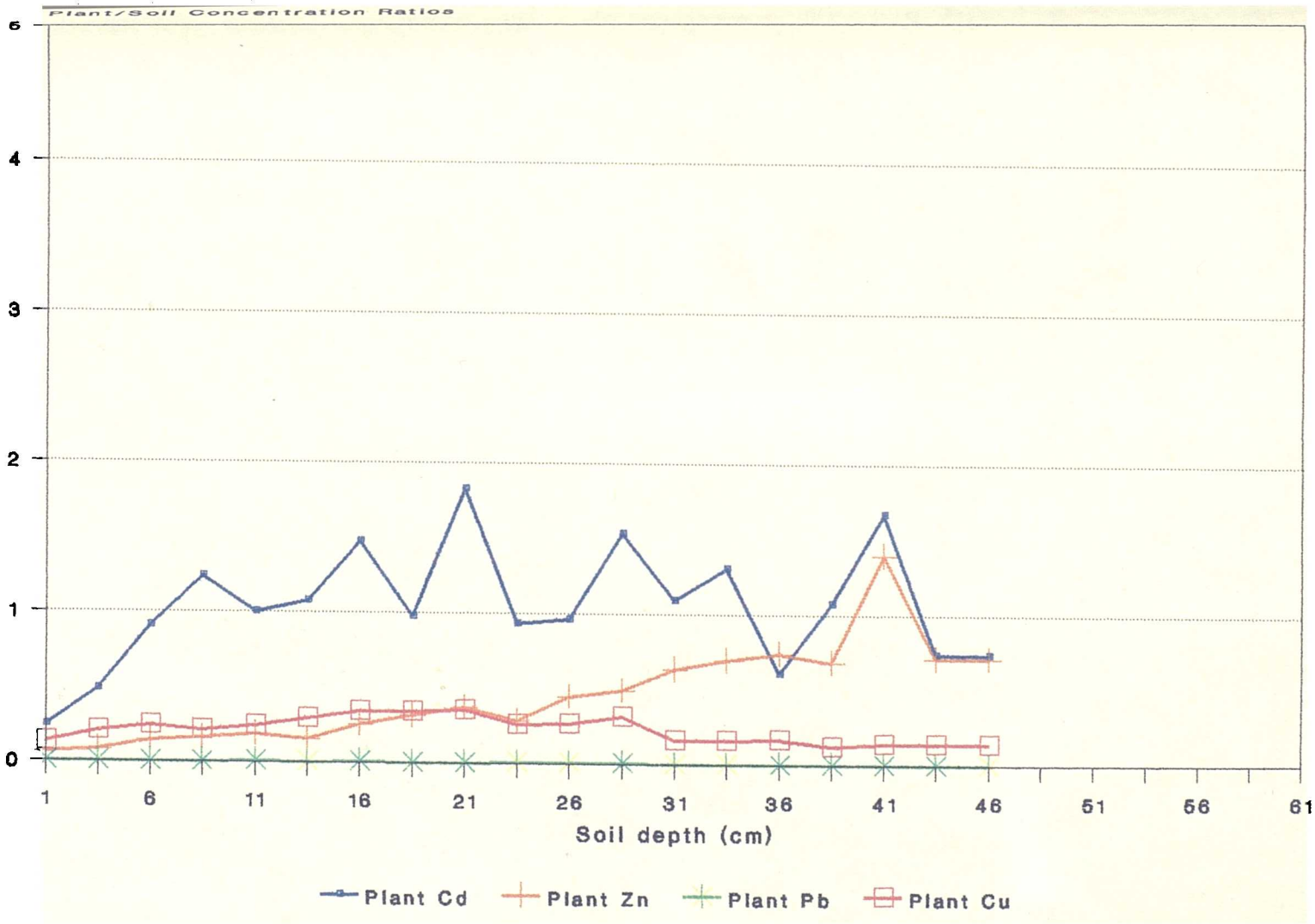


**Fig.5.3.2a Haw Wood Plant/Soil Ratios**
***Holcus lanatus***

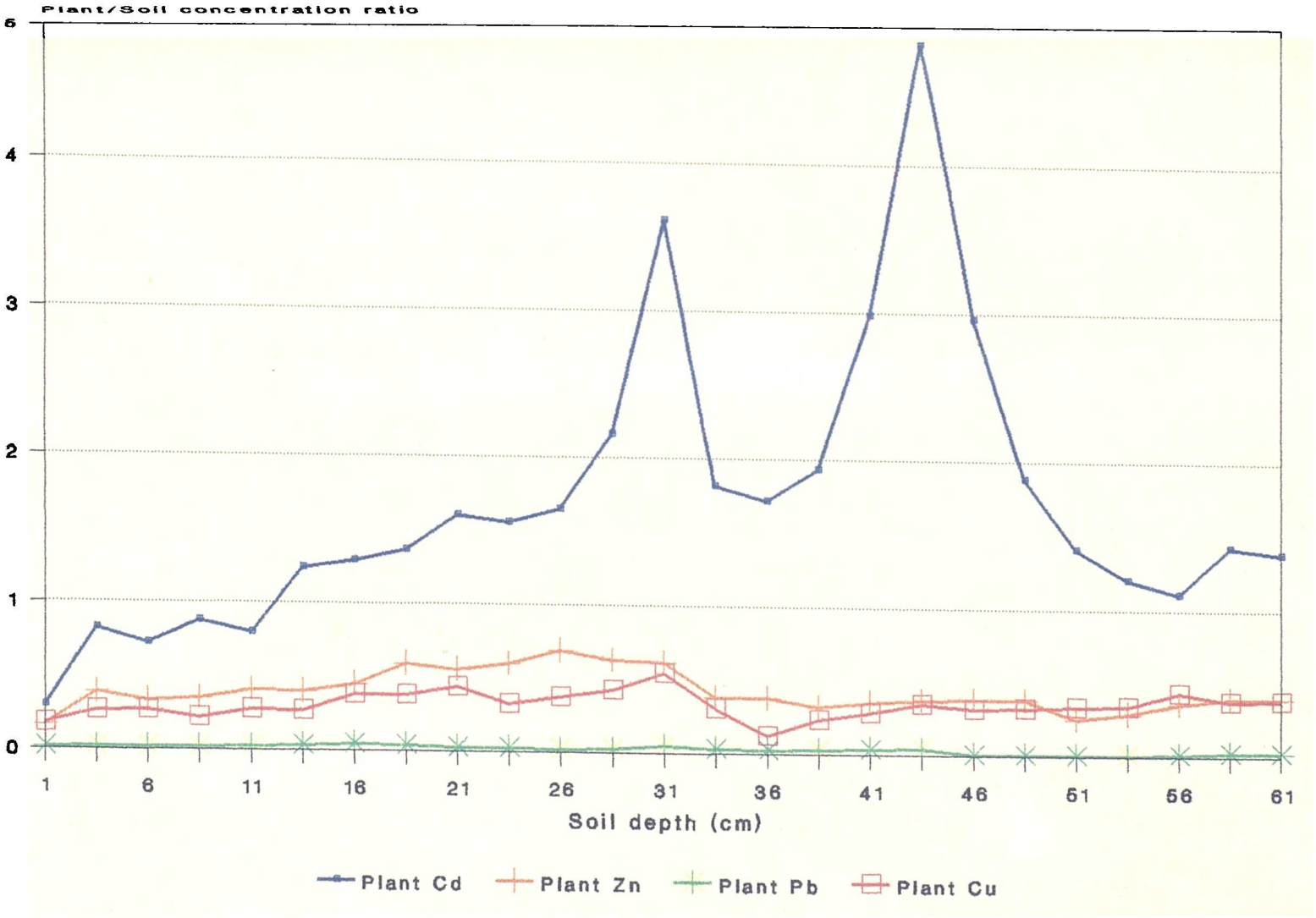


**Fig.5.3.2b Hallen Wood Plant/Soil Ratio**
***Holcus lanatus***

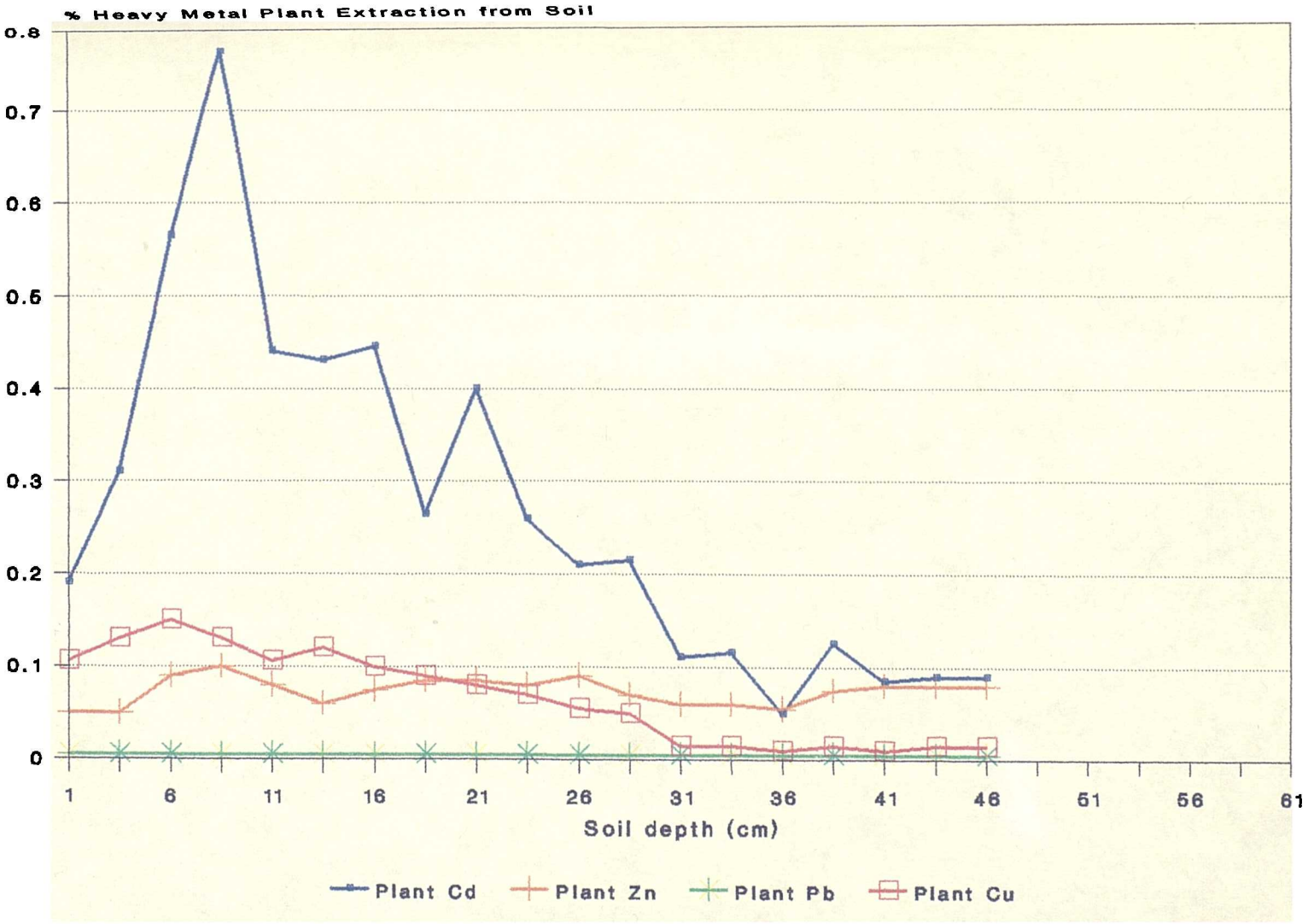


**Fig.5.3.3a Haw: Heavy Metal Uptake in *Holcus lanatus***

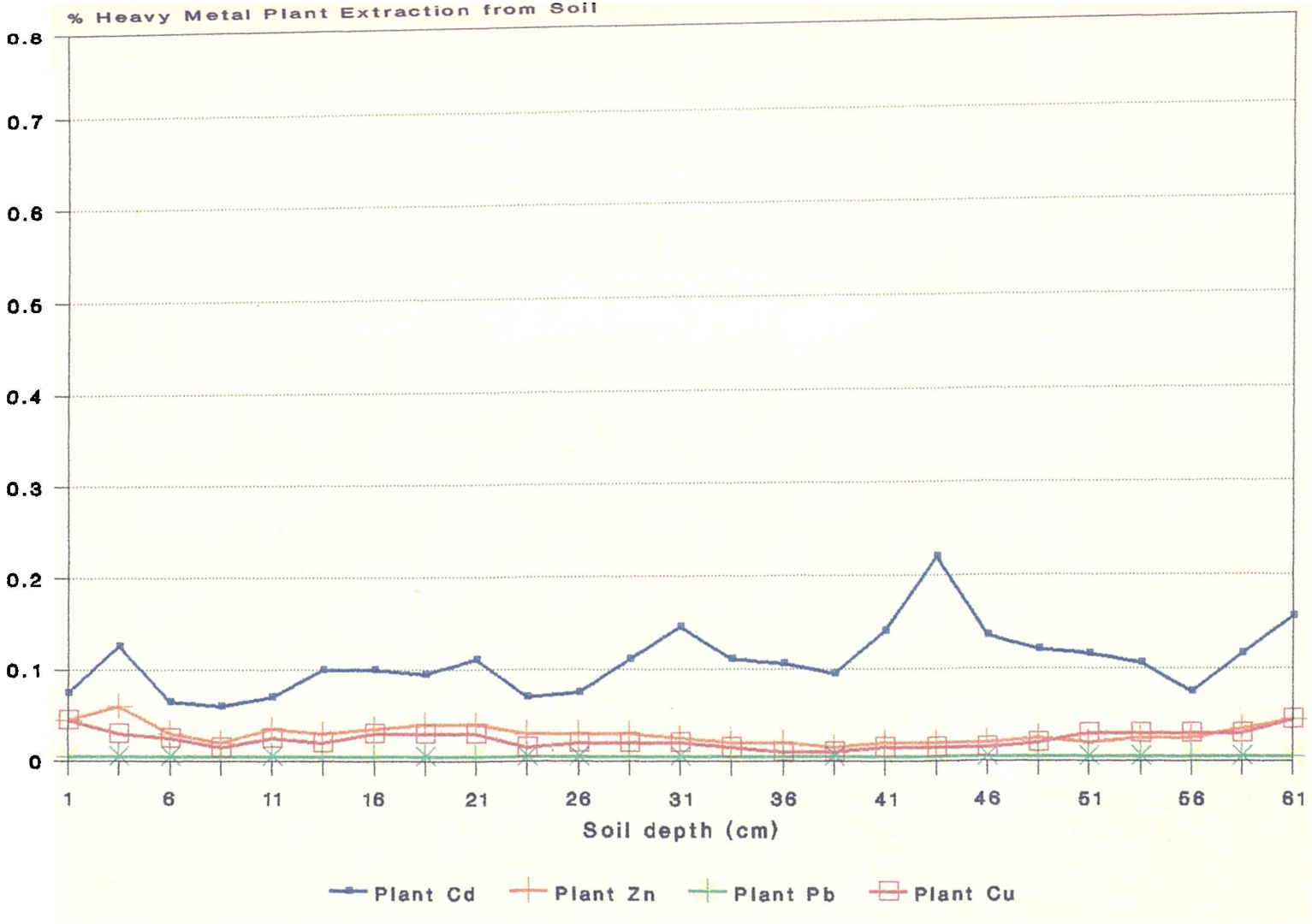


**Fig.5.3.3b Hallen: Heavy Metal Uptake in Holcus lanatus**

Table **5.3.2 Statistically Significant (p<0.1%) Pearson's Product Moment Correlation Coefficients of *Holcus lanatus* Metal Tissue Concentrations with Plant Height / Weight and Soil Extractable Metal Levels in Haw (n=17) and Hallen (n=24) Wood.**

| Haw Plant Conc. (mg/kg) | Plant Height | Plant Weight | Soil Available Metals Cd | Cu | Pb | Zn |
|---|---|---|---|---|---|---|
| Plant Cd | 0.730 | 0.908 | 0.927 | | | |
| Plant Cu | N.S. | N.S | | N.S. | | |
| Plant Pb | 0.767 | 0.730 | | | N.S. | |
| Plant Zn | N.S. | N.S. | | | | 0.779 |
| **Hallen Plant Conc. (mg/kg)** | | | | | | |
| Plant Cd | -0.816 | -0.693 | 0.663 | | | |
| Plant Cu | N.S. | N.S. | | N.S. | | |
| Plant Pb | N.S. | N.S. | | | 0.749 | |
| Plant Zn | -0.700 | N.S. | | | | 0.875 |

N.S. = not significant (p > 0.1%)

---

In Figs.5.3.2 and 5.3.3 for Haw profile grown plants, the former shows that the ratio of plant to soil concentration for Cd is *circa* 1.0 (1.05±0.40), whereas the latter graph shows that Cd extraction increases with decreasing depth from a base line level of 0.1% at 31-46cm depth to about 0.8% at 6-8.5cm depth. The decrease in ratios and percentage efficiency from 6cm to 0cm in both Figures could perhaps be a result of the higher toxic levels of Cd in the plant tissue (> 8 mg/kg Cd) and/or some other factor such as higher levels of organic matter (> 4% organic matter) in the soil. In the Hallen profile (Figs.5.3.2 and 5.3.3), Cd ratios of > 1 occur in mid-profile (Fig.5.3.2) with the two peaks at 28.5-31cm and 41-43.5cm depth reflecting the Cd tissue concentrations that occur in Fig.5.3.1. By taking the mass of the plants into account in Fig.5.3.3, the Cd peaks (especially the 28.5-31cm peak) are tremendously subdued in size. In fact, this last graph shows that the % efficiency of plant extraction is mainly about 0.1% throughout the entire Hallen profile which is comparable to the Haw profile at 28.5cm and deeper.

The height and weight of the plants at each depth down both soil profiles are illustrated in Fig.5.3.4. In the Haw plants, there was a general decline of plant height and weight with depth. Hallen plant height, in particular, appeared to be highly negatively correlated with Cd tissue concentrations in the assay plants ($r = -0.816$, Table 5.3.2). This perhaps suggests that the grass height was responding to cadmium toxicity within the plant tissues. The apparent recovery of height and weight at depth in the Hallen grown plants could be a result of lower heavy metal contamination within the soil (particularly with respect to "available" Cd and Zn).

Table 5.3.2 indicates that plant tissue concentrations of Cd and Zn tended to reflect the levels of available (total sequentially extractable or NRES) metals within the two soils. The same appears true for Pb in plants grown upon the Hallen soil profile. The negative relationship between plant Cd and plant height / weight for the Hallen soil probably indicates that phytotoxic concentrations of this metal existed within the Hallen grass tissues. The importance of Cd in plant dry weight / height reduction has been indicated in studies such as that of Lamoreaux and Chaney (1977). However, if the above is true then the positive relationship between plant Cd and plant height / weight for Haw Wood is somewhat intriguing.

Correlations between Hallen Cd and Zn variables (n = 24)

| | Plant Zn | NRES Zn | Plant Cd | NRES Cd |
|---|---|---|---|---|
| Plant Zn | 1.000 | | | |
| NRES Zn | 0.875 | 1.000 | | |
| Plant Cd | 0.715 | 0.449 | 1.000 | |
| NRES Cd | 0.916 | 0.936 | 0.663 | 1.000 |

Finally, perhaps one other aspect to consider is metal interaction. The correlation matrix shown above indicates that plant Zn is correlated highest with available (NRES) Cd rather than (NRES) Zn. However, plant Cd is correlated highest with it's own available pool of soil Cd (NRES Cd). Partial correlations ($r_{12.3}$), where $r_1$ and $r_2$ are correlated against each other with the third variable ($r_3$) being held constant, are given below:

| | $r_{12}$ | $r_3$ | Partial correlation coefficient |
|---|---|---|---|
| 1. | Plant Cd, NRES Cd | Plant Zn | 0.029* |
| 2. | Plant Zn, NRES Zn | Plant Cd | 0.887 |
| 3. | Plant Zn, Plant Cd | NRES Cd | 0.359* |
| 4. | Plant Zn, Plant Cd | NRES Zn | 0.745 |


Fig.5.3.4 Height and Weight of *Holcus lanatus*

| | | | |
|---|---|---|---|
| 5. | Plant Zn, NRES Zn | NRES Cd | 0.125* |
| 6. | Plant Cd, NRES Cd | NRES Zn | 0.772 |
| 7. | NRES Zn, NRES Cd | Plant Zn | 0.693 |
| 8. | NRES Zn, NRES Cd | Plant Cd | 0.954 |
| 9. | Plant Cd, NRES Zn | Plant Zn | 0.522 |
| 10. | Plant Zn, NRES Cd | Plant Cd | 0.844 |
| 11. | Plant Zn, NRES Cd | NRES Zn | 0.569 |
| 12. | Plant Cd, NRES Zn | NRES Cd | 0.651 |

* : not significant ($p > 5\%$)

From the above it would appear that any partial correlation containing the variables Plant Zn and NRES Cd has seen a decrease of $r_{12.3}$ in relation to the the simple correlation of $r_{12}$. The least significant partial correlations are 1, 3 and 5 where either Plant Zn or NRES Cd have been held constant. Therefore, there is some indication that Zn plant uptake and available soil Cd were associated with each other and that perhaps some form of Cd / Zn interaction has occurred: in particular with respect to the low $r_{12.3}$ values produced in 1 and 5 (which are highly non significant).

## 5.4. Consequences of Soil Acidification on the Uptake of Heavy Metals by Plants.

### 5.4.1. Introduction

The importance of this Section is that it illustrates the primary role of pH in controlling the bioavailability of Cd, Cu, Pb and Zn. Such changes in bioavailability are also envisaged within the different horizons of the soil profiles from Hallen and Haw which demonstrate variation in pH and heavy metal content. The consequences are that when a combination of higher heavy metal content and lower pH reaches the natural rooting depths of different species of plants, the potential for plant uptake is enhanced and coincidental entry to a wider / larger food chain becomes possible.

The soil profiles in Haw and Hallen Wood are open systems which have reacted accordingly to any change that they have been subjected to. In this Section, pH variation is described with respect to closed soil-plant systems. The slurry system described in Chapter 4 Section 3 demonstrated that pH change affected metal solubility such that a curvilinear response was created. The same curvilinear response ought to be maintained where acidification has been induced within closed plant-soil systems. However, the signature of response could very much depend upon a number of factors e.g. the plant

species used, soil type, level of metals used, form of metals used, maintenance of the experiment and length of time of experiment.

## 5.4.2. Materials and Methods

The investigation was conducted as a pot experiment under greenhouse conditions. The soil used was a Mendip loam soil, pre-sterilized, with a pH of about pH6.5. Pre-treatment test pots of soil were used to assess how much dilute $H_2SO_4$ or CaO was required to adjust the pH of the soil to various different levels. The chosen required pH levels were 3.75, 4.75, 5.25, 5.75, 6.25, 7.00 and 8.00. However, as is demonstrated in Fig.5.4.1, maintenance of strict pH levels throughout the experiment was an impossible task. The amount of acid-S or lime needed to adjust the original soil pH to the required levels was initially predetermined. The original metal levels (Cd, Cu, Pb and Zn) within the soil were 1.1 (±0.3) mg/kg Cd, 21.6 (±1.5) mg/kg Cu, 327 (±35) mg/kg Pb and 352 (±16) mg/kg Zn on a dry soil basis (standard deviation in parenthesis). Four treatments of metal levels were used: a control where no metals were added; where only an addition of 100 mg/kg CdO was made; where only an addition of 250 mg/kg ZnO was made; and where only an addition of 750 mg/kg PbO was made. The additions of metals were made on a dry soil weight basis. No fertilizer additions were made to the soils.

With four different metal treatments at 7 different pH levels and each pH level being replicated 10 times, 280 4.5" pots in total were required and 280 sunflower seedlings (*Helianthus annuus*) were planted (i.e. one per pot). The above ground parts of the plants were harvested after 6 weeks of growth; plant material being taken above the first cotelydons in case any soil splash had occurred during watering. Soils were watered with deionised water only. Damp soil was measured for pH with a surface soil pH meter during the course of the experiment (see Fig.5.4.1), although the initial soil pH's were measured with a glass electrode in a 1:2.5 soil water paste. Prior to harvesting, the plant heights were measured from the top of the pot rim to the growing apex (as vertical height in centimetres).

Once harvested, the above ground parts of the plants were dried in an oven at 80°C, weighed (dry weight), digested in concentrated Analar nitric acid and metal concentrations (Cd, Cu, Pb and Zn) measured by flame AAS (see Appendix A). Due to the nature of the loamy soil and the robust nature of the sunflower roots, the roots were washed and separated from the soil.

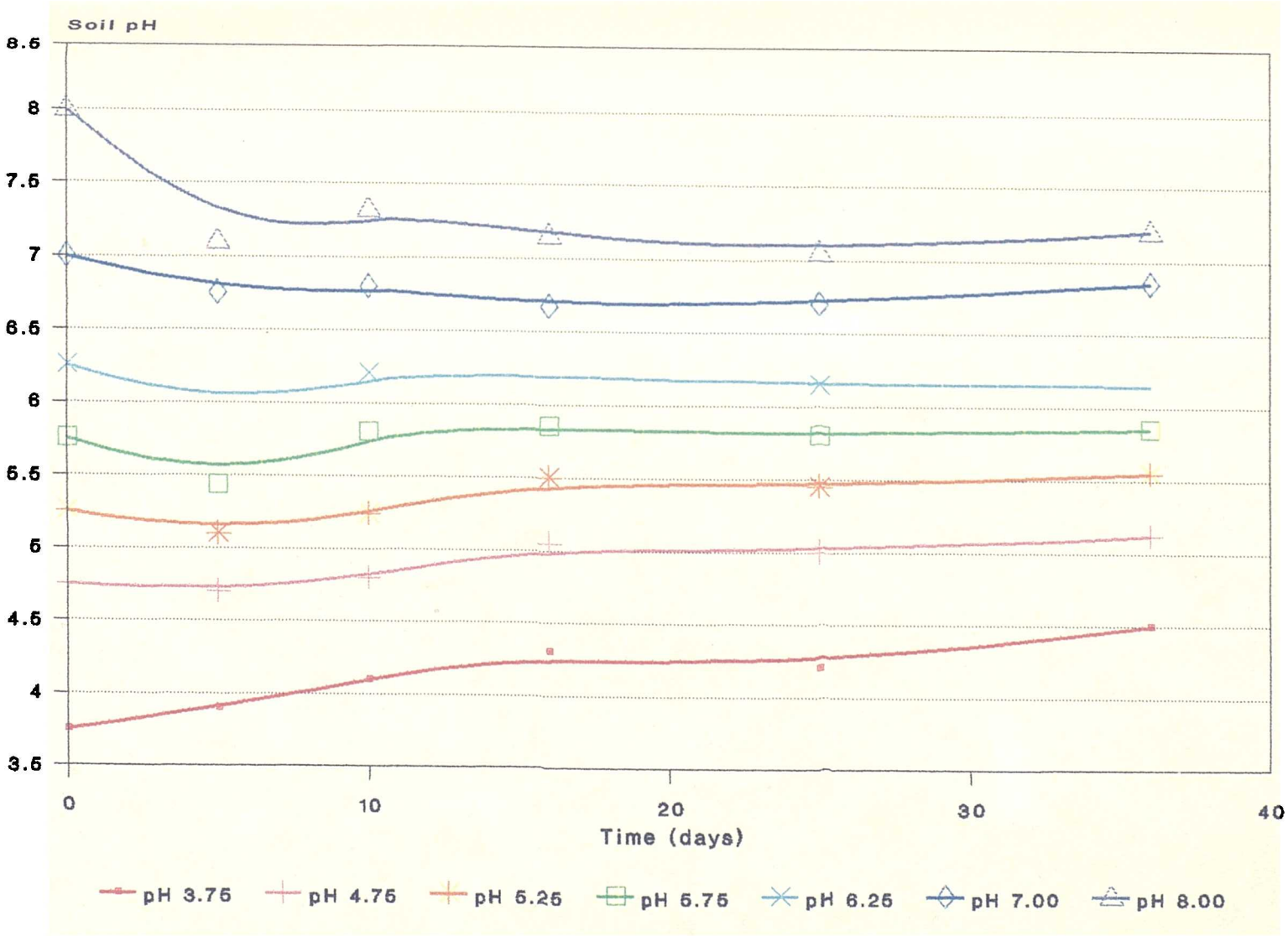


**Fig.5.4.1 pH Change with Time for all Four Metal Treatments**

The roots and the lower stem node leading the cotyledons were then separately dried in the oven at 80°C and weighed.

## 5.4.3. Effect of Soil pH on Cd, Cu, Pb and Zn Uptake by Sunflower Plants

Fig.5.4.2(a-c) illustrate the effect of pH on metal uptake by sunflower plants. As might be expected, the uptake of Cd (Fig.5.4.2a) was far greater from the soils which were treated with higher levels of Cd at all levels of pH. The lowest pH level to which a soil has to be limed in order to overcome heavy metal contamination is a function of both the type and the concentration of the metal (Albasel and Cottenie 1985), and hence plant uptake is likely to be affected accordingly. There was a relatively linear response of plant Cd mg/kg uptake in relation to pH over the range of pH3.75-6.25 in the 100 mg/kg Cd treatment grown plants. Standard error bars shown for the 100 mg/kg Cd treatment plants suggest that there were significant differences in the mean Cd plant tissue concentrations between the different pH levels. Figs.5.4.2b and 5.4.2c show similar responses to pH for Zn and Pb uptake.

Fig.5.4.1 indicates that although distinct differences between pH levels were maintained with time, there was a distinct tendency for the soil to buffer against the pH changes applied. This feature was most prominent in the lowest and highest pH levels: the pH8 level decreased by as much as *c.* one unit of pH and the pH3.75 level increased by a similar amount. However, this might have been an artifact between the differences in technique used to measure the initial soil pH (via a 1:25 soil: deionised water paste) and the pH's thereafter (via a surface soil contact pH probe). The fact that Zn uptake pertains near linearity to pH7.0 in Fig.5.4.2b could be explained as Zn (in terms of plant uptake) is assumed to have intermediate-high mobility, and plants usually reflect changes in the Zn content of growth media (Kabata-Pendias and Pendias 1984). As Zn is relatively mobile in relation to Cu and Pb (see Section 5.2.3) and occurs in the Zn treated soil at about 600 mg/kg, then it seems likely that more plant available Zn was in existence even at the higher pH levels.

Fig.5.4.2a-c demonstrate the effect of pH on plant uptake for high levels of Cd (101 mg/kg), Zn (602 mg/kg) and Pb (1077 mg/kg) whereby additions of these metals have been made to the soil. Fig.5.4.3a-d show a similar signature of response for those metals in the various treatments whose levels have not been altered from their natural levels. The natural levels of Zn (352

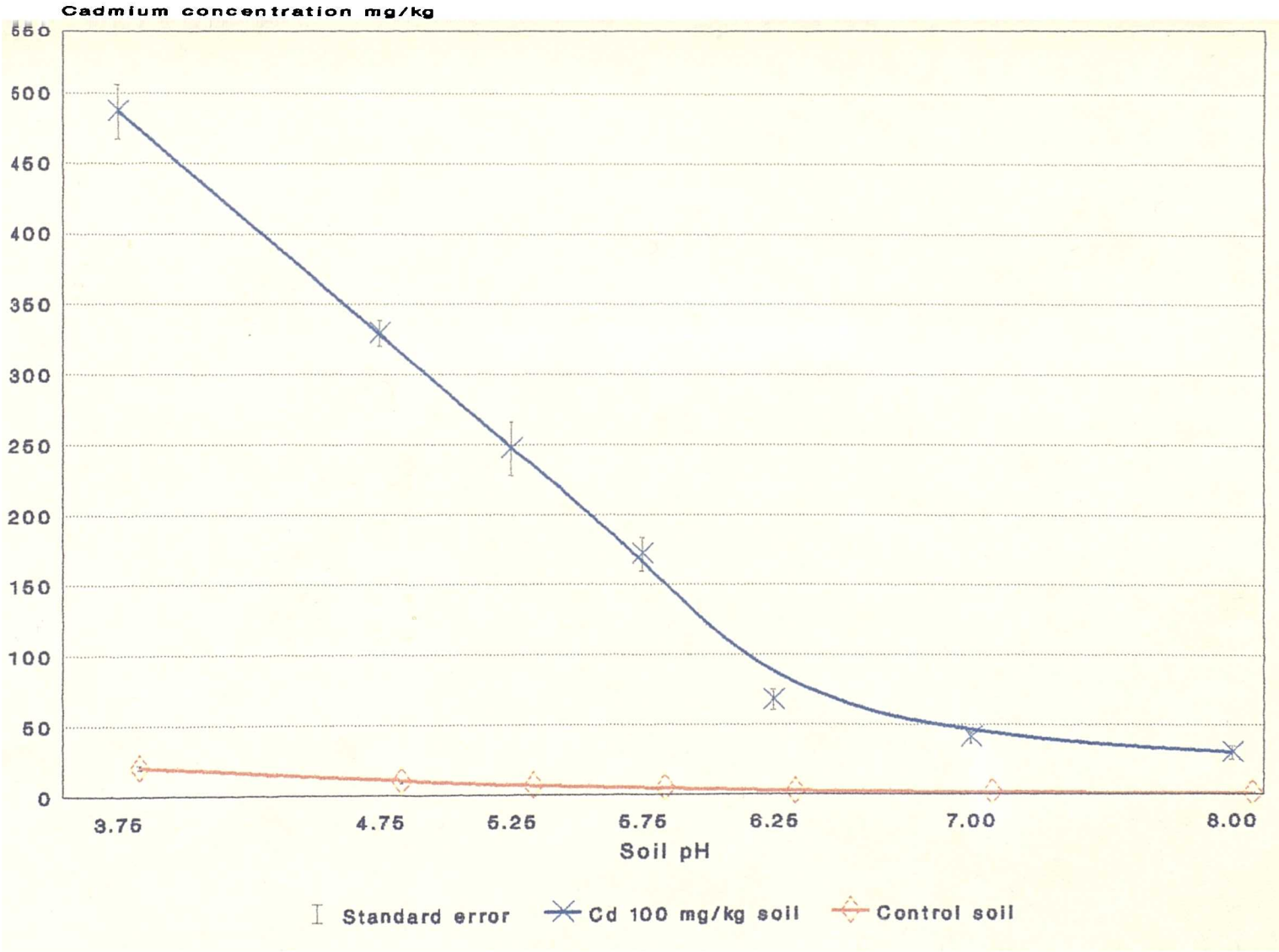


**Fig.5.4.2a Sunflower: Cadmium Uptake**

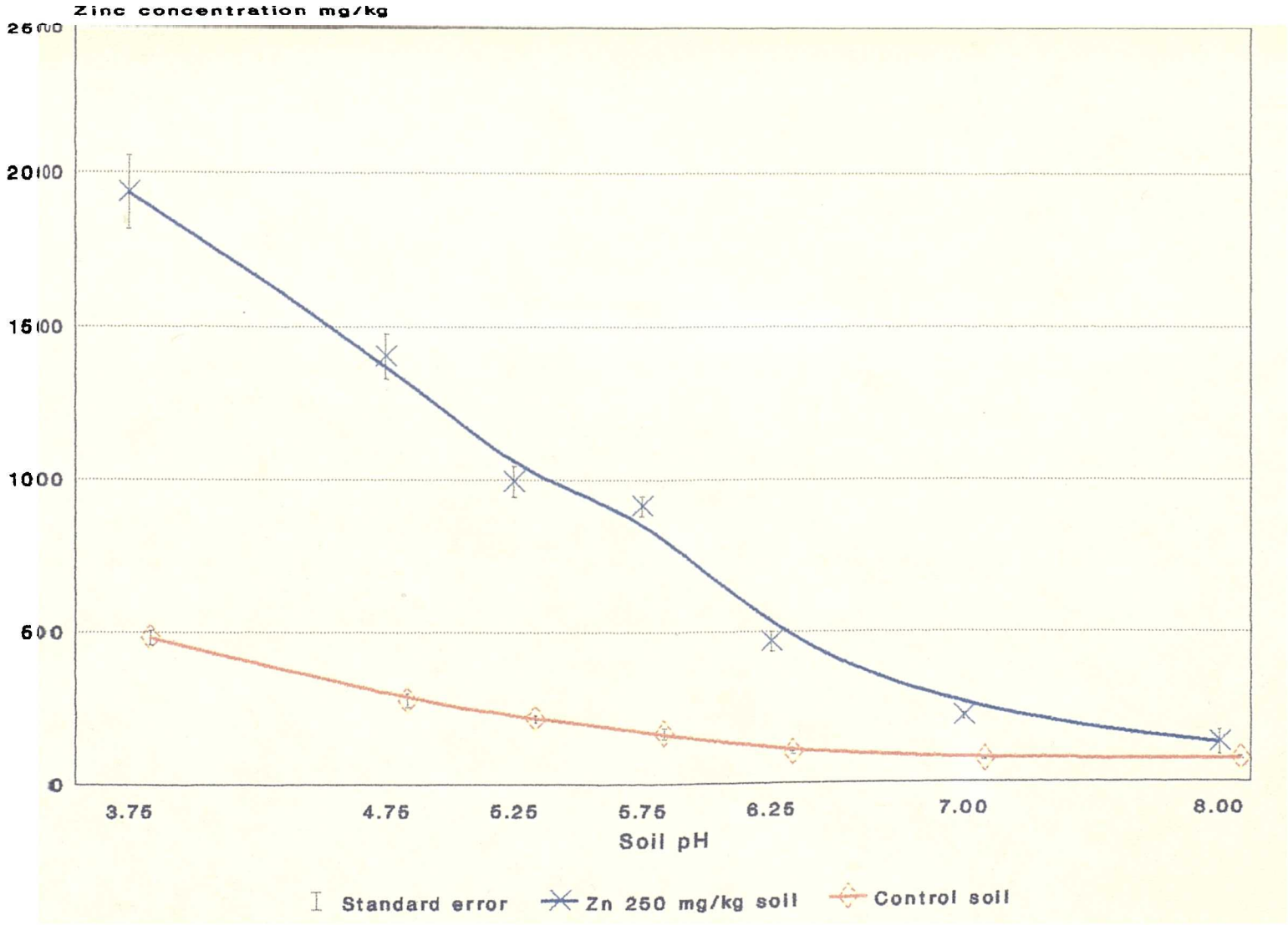


Fig.5.4.2b Sunflower: Zinc Uptake

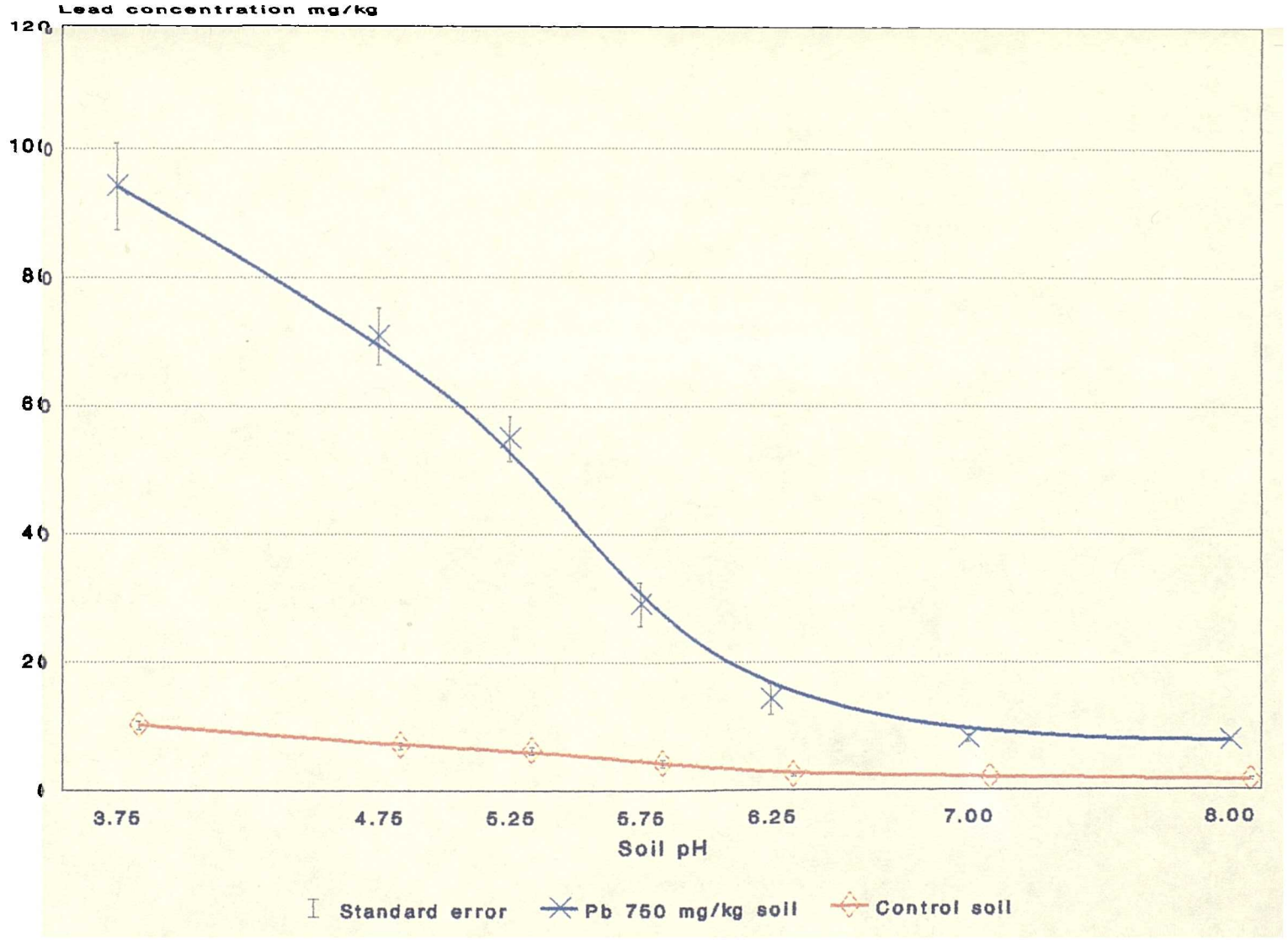


Fig.5.4.2c Sunflower: Lead Uptake

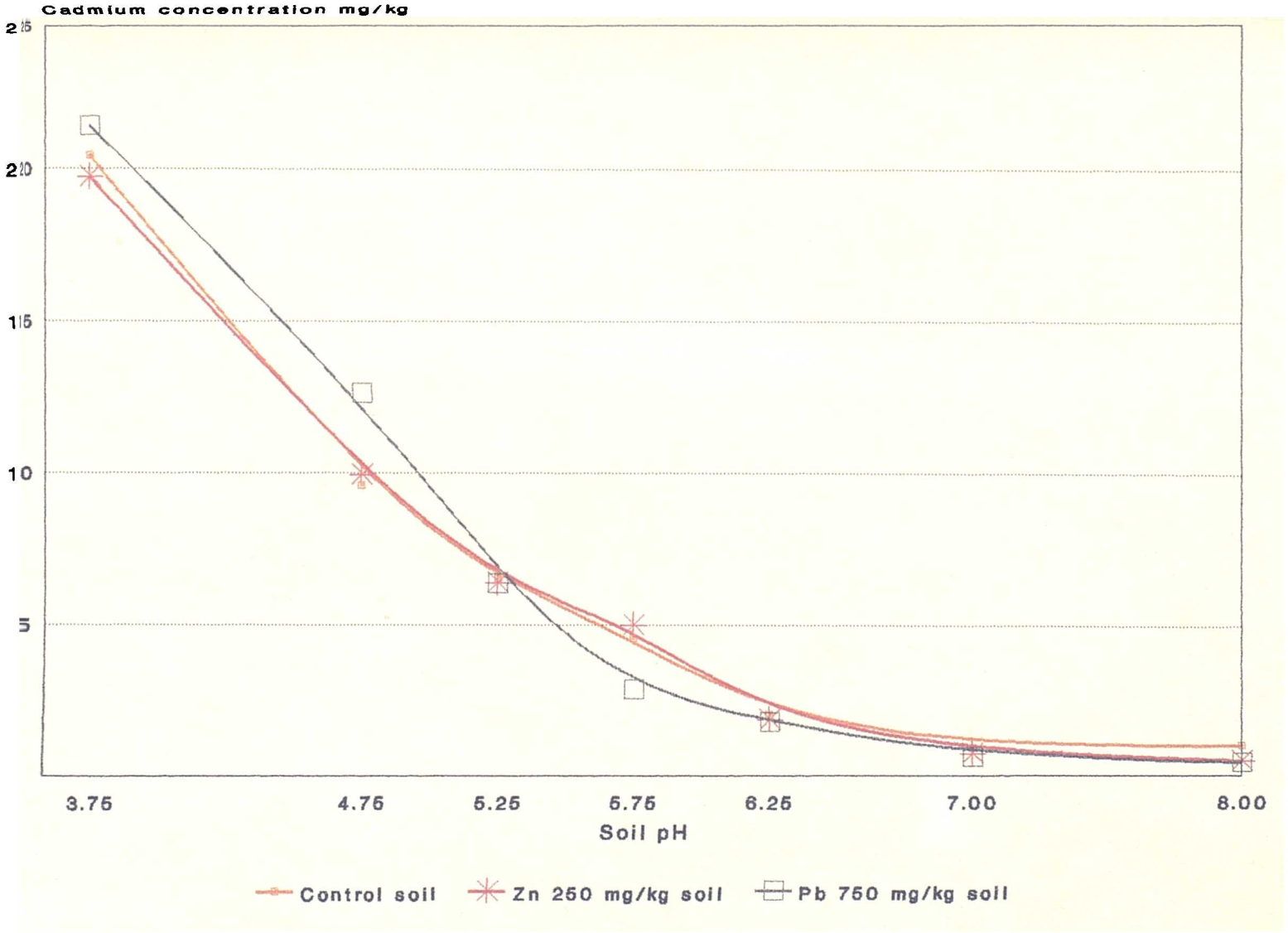


**Fig.5.4.3a Sunflower: Cadmium Uptake**

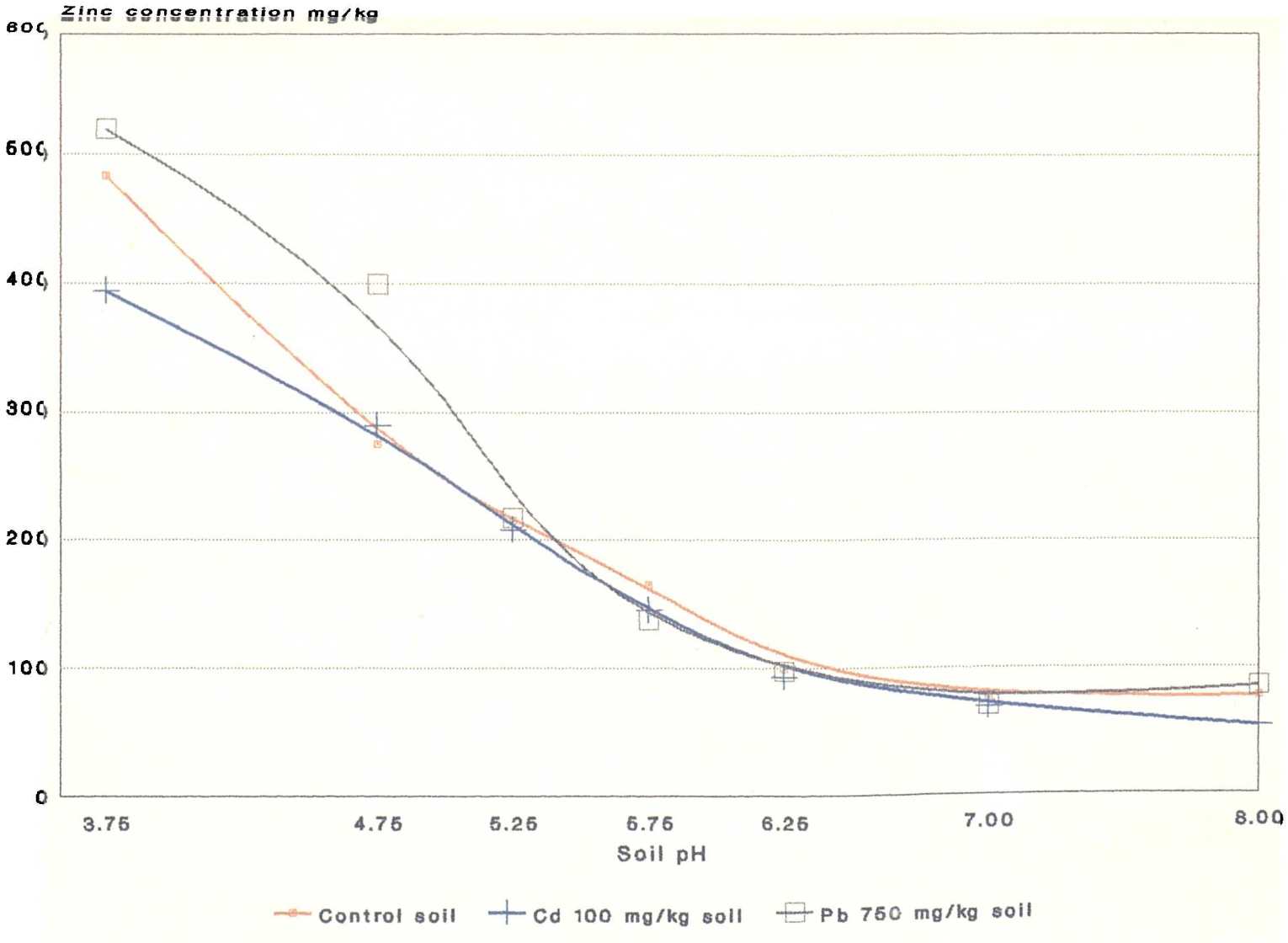
Zinc concentration mg/kg
600
500
400
300
200
100
0
3.75
4.75
5.25
5.75
6.25
7.00
8.00
Soil pH
Control soil
Cd 100 mg/kg soil
Pb 750 mg/kg soil

Fig.5.4.3b

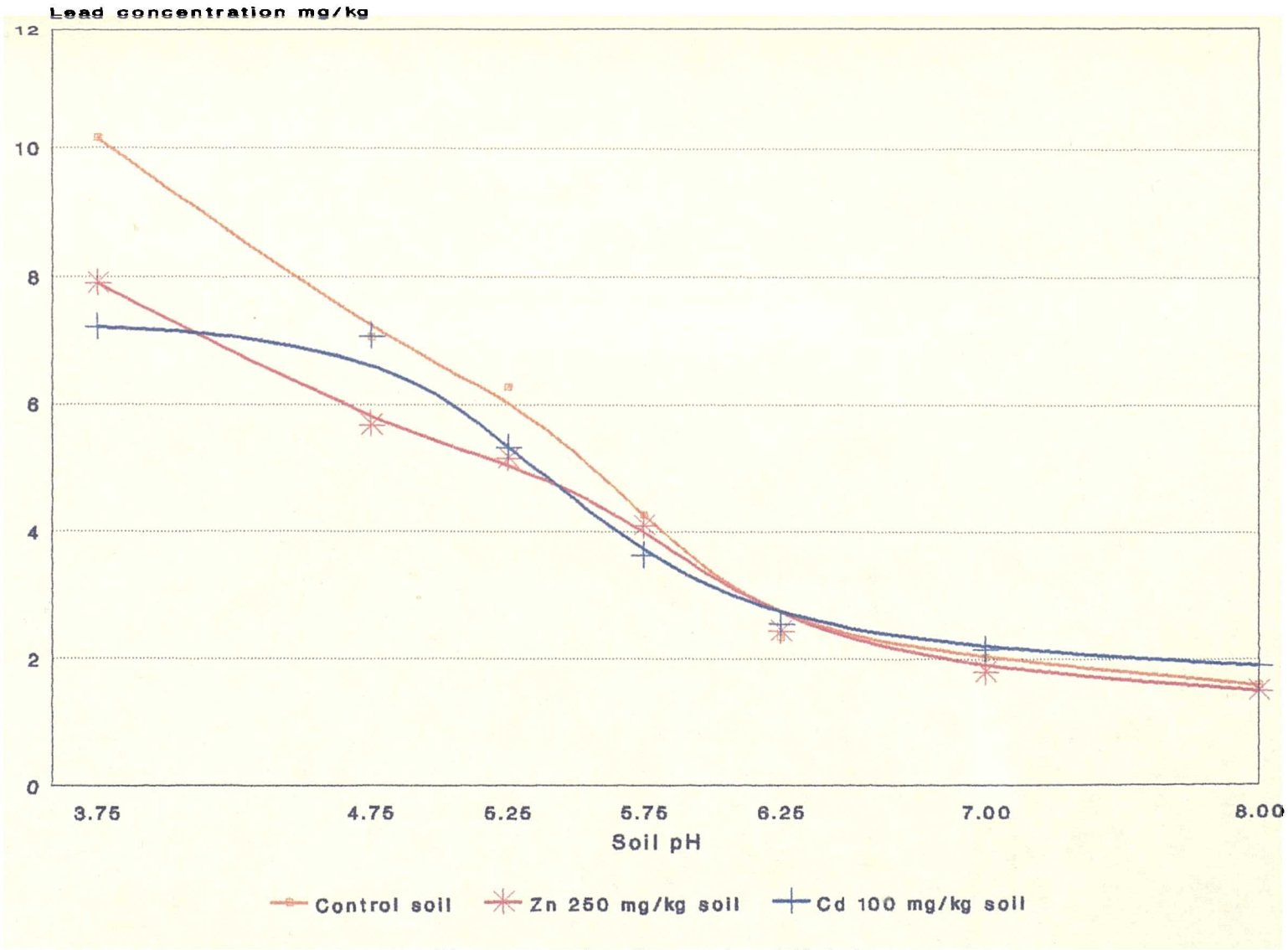


**Fig.5.4.3c Sunflower: Lead Uptake**

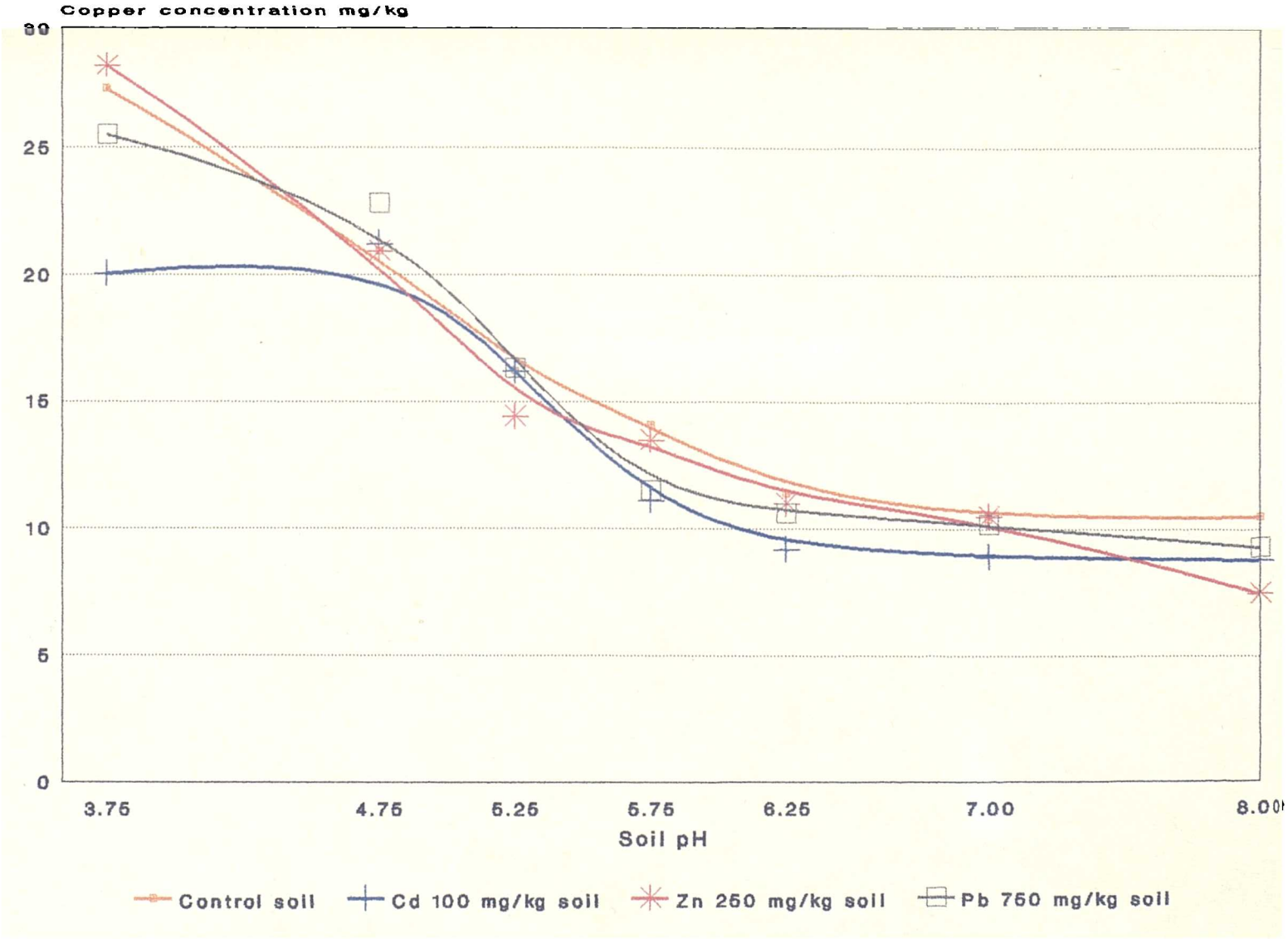


**Fig.5.4.3d Sunflower: Copper Uptake**

mg/kg) and Pb (327 mg/kg) were still quite high for the normal concentrations expected in British soils (see Chapter 2, Section 2.2). This was especially true of Pb. However, Cd and Cu occurred at levels normal for British soils. The graphs seem to illustrate that the uptake response was reproducible (despite the different levels of metal treatment) especially at pH>5. At pH<5 (more especially at pH3.75) factors such as Cd toxicity might have affected the plant tissue concentrations of other metals. Hence, in Fig.5.4.3c-d for Pb and Cu, the Cd treated soils demonstrate a sigmoidal response. Any effect of Cd toxicity upon Zn uptake appears less evident at pH3.75 and was possibly as a result of the relative mobility of Zn in its uptake by plants in relation to Cu and Pb. Such mobility within plants also extends to Cd as well as Zn (Balsberg 1989); and Cd uptake in Fig.5.4.3a appears to be similar at all pH levels whatever the metal level treatment (excluding, of course, the Cd 100 mg/kg treatment).

Student's t-test values indicate that Cd plant concentrations in Fig.5.4.3a only significantly deviated from the control Cd plant concentrations under the Pb treatment at pH7.0 ($t = 2.64$, $p < 2\%$) and pH8.0 ($t = 482$, $p < 0.01\%$), and the Zn treatment at pH8.0 ($t = 4.49$, $p < 0.01\%$). Similarly, Cu concentrations were significantly different from the control Cu plant concentrations in Fig.5.4.3d under the following treatments and pH's:

| | | |
|---|---|---|
| Cd treatment : | pH 3.75 | ($t = 3.97$, $p < 1\%$) |
| | pH 5.75 | ($t = 3.14$, $p < 1\%$) |
| | pH 6.25 | ($t = 2.86$, $p < 2\%$) |
| | pH 7.00 | ($t = 2.60$, $p < 2\%$) |
| | pH 8.00 | ($t = 2.03$, $p = 6\%$) |
| Zn treatment : | pH 8.00 | ($t = 3.63$, $p < 1\%$) |
| Pb treatment : | pH 5.75 | ($t = 2.50$, $p < 5\%$) |

Zn plant concentrations were significantly different from their control Zn plant concentrations in Fig.5.4.3b under the Cd treatment at pH3.75 ($t = 3.33$, $p < 1\%$) and pH8.0 ($t = 4.18$, $p < 0.1\%$). Finally, Pb plant concentrations were significantly different from their control Pb plant concentrations in Fig.5.4.3c under the Cd treatment at pH3.75 ($t = 3.46$, $p < 1\%$).

From such t-values the effect of the Cd treatment (and associated Cd toxicity) at pH3.75 in reducing Cu, Pb and Zn concentration uptake in the plants gains further support. Also at 5 of the 8 pH levels, the Cd treatment appeared to be influential in reducing Cu uptake in relation to the control Cu

plant concentrations. The matter of metal treatment effect and plant growth is given further consideration in the next section.

To gain a better understanding of the effect of pH on the sunflower uptake of metals, analysis of variance was used to assess whether the mean concentrations of Cd, Cu, Pb or Zn in the plants were equal at all pH levels. The results in Table 5.4.1 suggest that the differences in the plant metal concentration between the seven levels of pH treatment were significant for all the metal treatments shown.

The effect of decreasing soil pH and increasing plant uptake of heavy metals is not an original concept (e.g. Andersson and Nilsson 1974, Berrow and Burridge 1979, Eriksson 1989, Xian and Shokohifard 1989). The addition of lime to acid soils in order to reduce heavy metal uptake in plants is often advocated (e.g. Albasel and Cottenie 1985, Page *et al.* 1981). Modification in soil pH levels are usually achieved by the addition of lime or sulphur depending upon the pH level that is required (Albasel and Cottenie 1985). Thus, under acceptance of the fact that anions (e.g. $SO_4^{2-}$) or cations (eg. $Ca^{2+}$) have also to be added to the soil system in order to change the soil pH, then the results in this section indicate that acidification of soils can be important in affecting heavy metal uptake by plants. More importantly, within the design of the experimentation of the plant-soil system used, the pH effect has been seen to occur over 0.5pH unit increments between pH4.75 to pH6.25, which has helped to emphasize the lower rate of metal uptake by plants between *c.* pH6-8 over the 6 weeks of growth. The exception to this was the Zn uptake in the Zn treated soil. Apart from the latter exception, the importance of maintaining pH levels in soils at pH6.5 or greater (see Section 5.2.1) to reduce plant metal uptake was illustrated within the experimental system.

It is stressed that the outcome of the "signature of response", as regards pH effect on metal uptake in plants, depends upon the interaction of the soil-plant-metal system (see Section 5.2.7 and Fig. 5.2.7). Using a plant such as sunflower (with a high rate of biomass production) and using a reasonably high level of replication per treatment (i.e. at least ten sample plants per pH treatment), the plant appears to be very useful as a test crop plant.

**Table 5.4.1 Analysis of variance of pH level effects on plant Cd, Cu, Pb or Zn concentrations according to the various metal treatments (source DF = 6; p value=degree of significance).**

| | Metal Uptake by Plants | Metal Treatment | DF in Error | DF in Total | F-ratio | p value |
|---|---|---|---|---|---|---|
| 1. | Cd | Control | 63 | 69 | 54.09 | p < 1% |
| 2. | Cd | 100ug/gCd | 63 | 69 | 188.98 | p < 1% |
| 3. | Cd | 250ug/gZn | 63 | 69 | 79.86 | p < 1% |
| 4. | Cd | 750ug/gPb | 63 | 69 | 60.82 | p < 1% |
| 5. | Cd | Control+ 250ug/gZn+ 750ug/gPb | 203 | 209 | 188.78 | p < 1% |
| 6. | Cu | Control | 63 | 69 | 35.42 | p < 1% |
| 7. | Cu | 100ug/gCd | 63 | 69 | 20.40 | p < 1% |
| 8. | Cu | 250ug/gZn | 63 | 69 | 39.47 | p < 1% |
| 9. | Cu | 750ug/gPb | 63 | 69 | 39.97 | p < 1% |
| 10. | Cu | Control+ 100ug/gCd+ 250ug/gZn+ 750ug/gPb | 273 | 279 | 114.28 | p < 1% |
| 11. | Zn | Control | 63 | 69 | 95.23 | p < 1% |
| 12. | Zn | 100ug/gCd | 63 | 69 | 220.08 | p < 1% |
| 13. | Zn | 250ug/gZn | 63 | 69 | 103.52 | p < 1% |
| 14. | Zn | 750ug/gPb | 63 | 69 | 135.05 | p < 1% |
| 15. | Zn | Control+ 100ug/gCd+ 750ug/gPb | 203 | 209 | 298.52 | p < 1% |
| 16. | Pb | Control | 63 | 69 | 49.99 | p < 1% |
| 17. | Pb | 100ug/gCd | 63 | 69 | 15.58 | p < 1% |
| 18. | Pb | 250ug/gZn | 63 | 69 | 14.23 | p < 1% |
| 19. | Pb | 750ug/gPb | 63 | 69 | 85.51 | p < 1% |
| 20. | Pb | Control+ 100ug/gCd+ 250ug/gZn | 203 | 209 | 62.04 | p < 1% |

Nos.1-4, 6-9, 11-14, 16-19 contain 10 sample items per pH level treatment.
Nos.5, 15 and 20 contain 30 sample items per pH level treatment.
No.10 contains 40 sample items per pH level treatment.

## 5.4.4. Effect of Metal Levels and pH Adjustment upon the Growth and Metal Content of the Sunflower Plants.

Figs.5.4.4-5.4.6 illustrate the plant weights recorded for each treatment. The tolerance indices shown demonstrate the growth of the plants normalised with respect to growth in the control system. This quantitative effect has been produced by use of the tolerance index (ti) (Cottenie 1980) whereby:

$$ti = \frac{\text{growth of plant in enriched medium}}{\text{growth of plant in normal medium}}$$

The shoot weight comprises the weight of the above ground parts of plants used for digestion and analysis plus the lower stem section not used in the chemical analysis.

The general overview is that within the soil used and the various metal level treatments used, the optimum growth of the plants would appear to have been in the pH5.75-7.00 range, although the control plants maintained more consistent growth over the pH4.75-8.00 range (Figs.5.4.4-5.4.6). In terms of peak mass production, the optimum total weight produced by control plants occurred at pH5.75, whereas those soils treated with high Cd, Zn, Pb levels favoured the pH6.25 level for optimum weight production.

The tolerance indices in Figs.5.4.4-5.4.6 indicate that conditions were more adverse to roots than to shoots in Cd, Pb and Zn treated soil. Clearly, the most acid conditions were the most stressful / toxic where Cd, Zn and Pb have been added to soils: leaf chlorosis was the most obvious symptom that occurred in a number of plants especially in Cd and Zn treatments at pH3.75. The same Figures also demonstrate that high Cd, Pb and Zn additions and high soil pH (pH8.0) were also not beneficial to plant growth. No obvious toxicity symptoms were apparent in the leaves of plants (such as chlorosis, necrosis, curling, browning, reddening etc.). Stunting / reduction in plant height was the most obvious symptom in the Cd treatment plants.

Figs.5.4.4-5.4.6 also illustrate that the Cd treatment clearly had the most deleterious impact upon the sunflower growth. The Pb and Zn treatments both maintained a similar stress impact upon the sunflower plants. However, it seems that at pH6.25 and pH7.00 the Zn treatment was almost beneficial towards plant shoot growth; whereas between pH5.75 and pH8.0 Pb would appear to have created no reduction in shoot weight (see Fig.5.4.5). In the case of the Pb treatment, this was despite the reduction in root weight

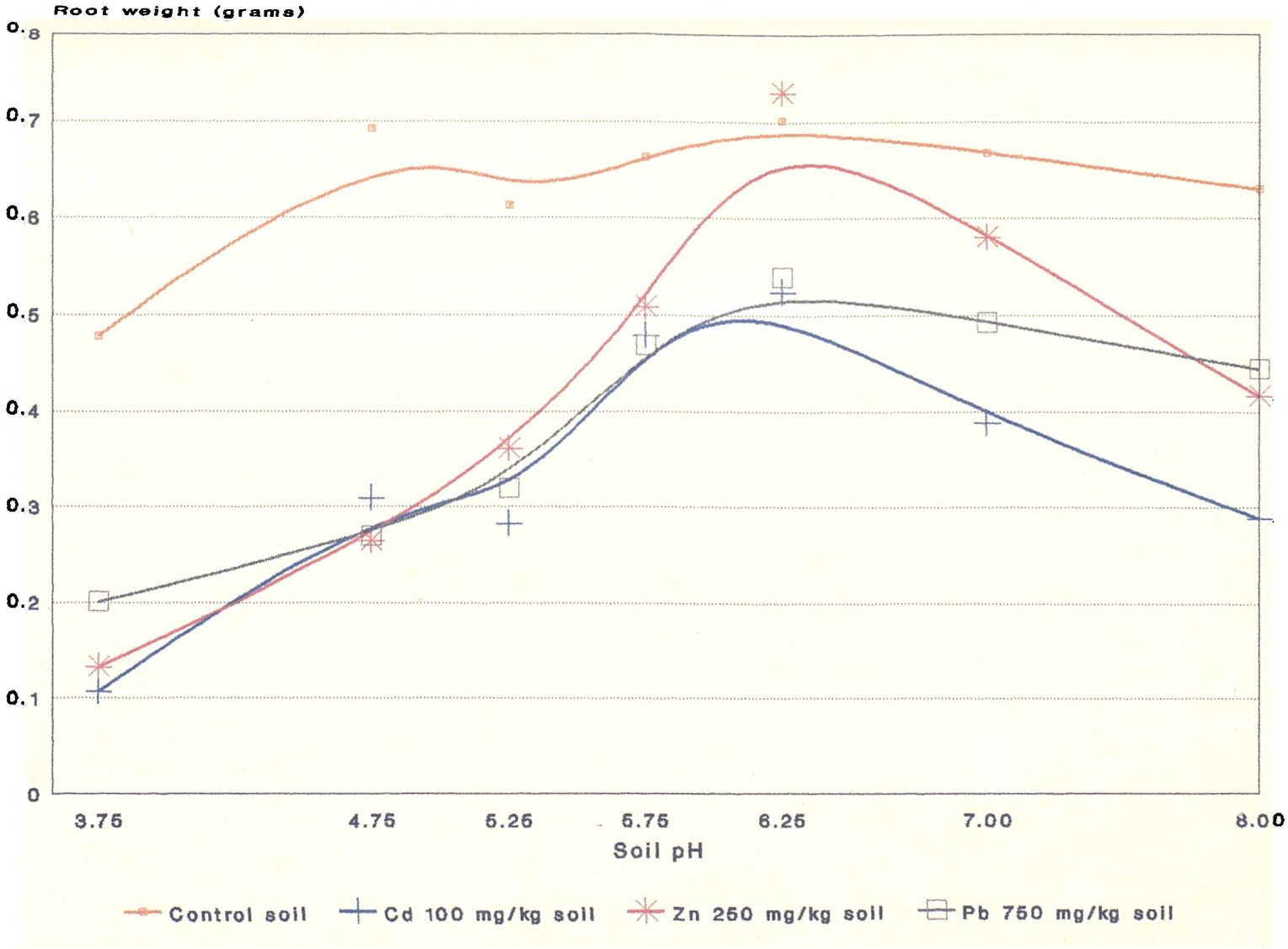


**Fig.5.4.4a Sunflower: Root Weight**

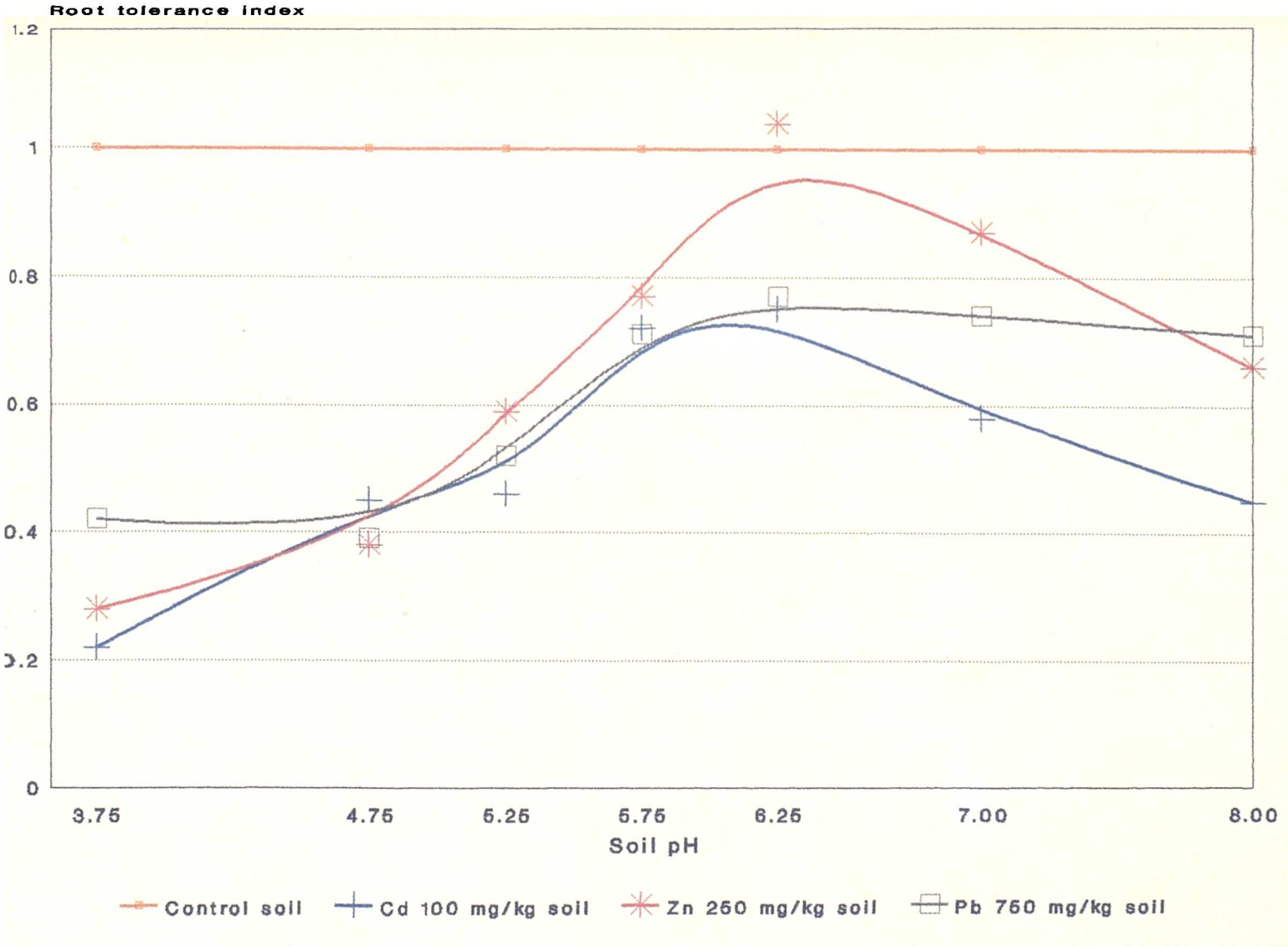


Fig.5.4.4b Sunflower: Root Tolerance

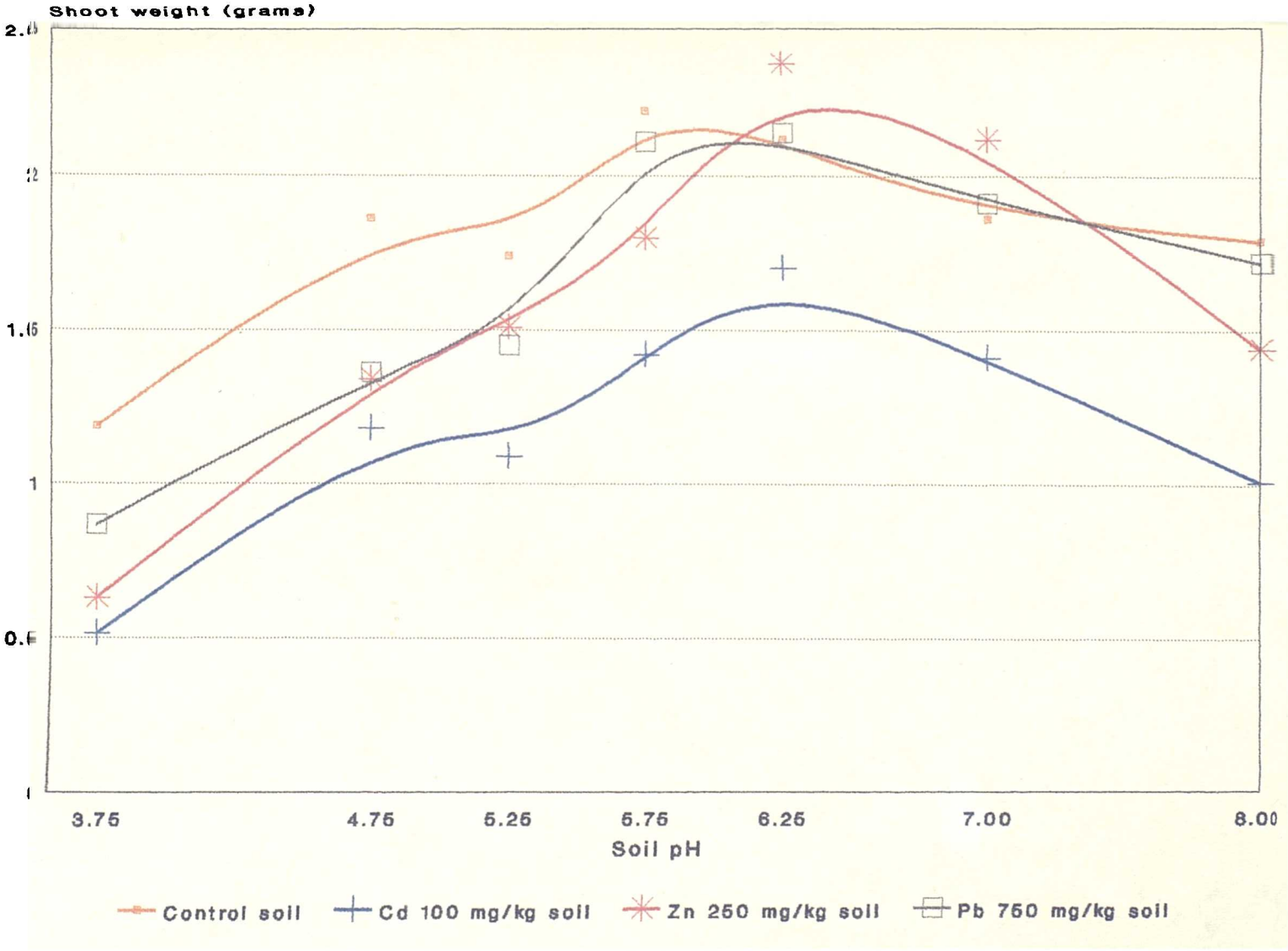


Fig.5.4.5a Sunflower: Shoot Weight


**Fig.5.4.5b Sunflower: Shoot Tolerance**

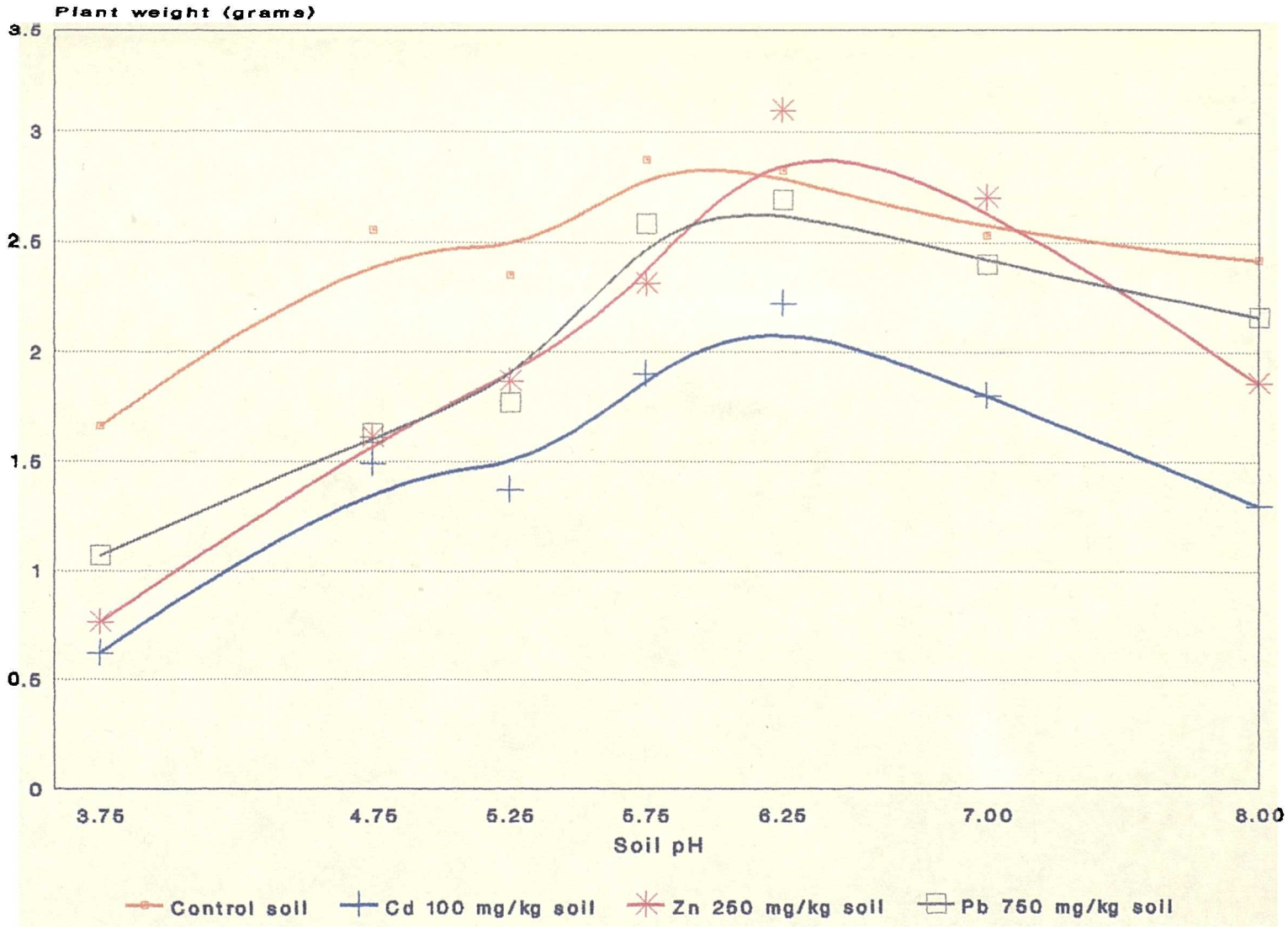


**Fig.5.4.6a Sunflower: Plant Weight**

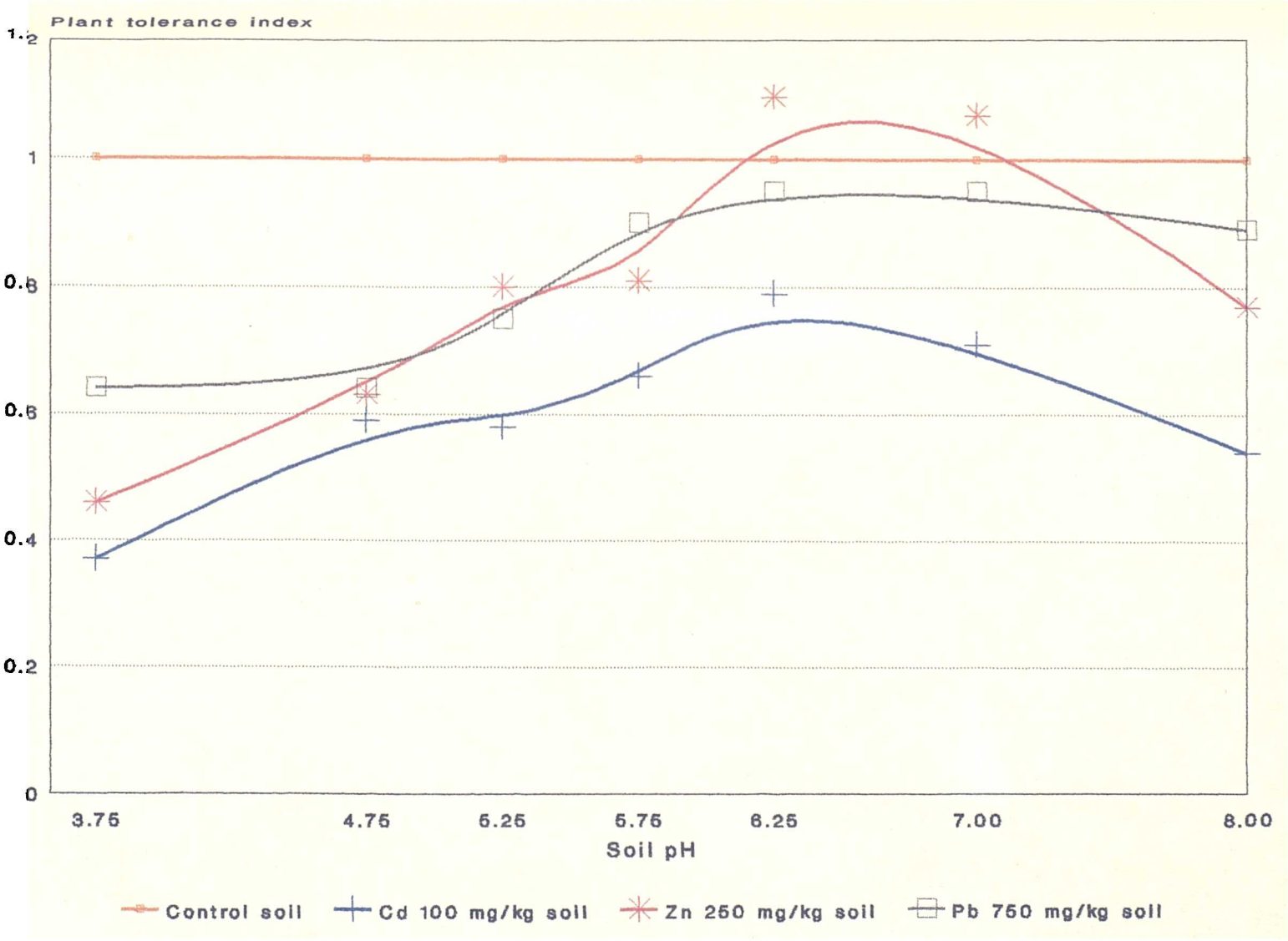


**Fig.5.4.6b Sunflower: Plant Tolerance**

(Fig.5.4.4). As the concentration of Pb in the Pb treated soil (1077 mg/kg) was almost twice as high as the Zn in the Zn treated soil (602 mg/kg) it is possible to surmise that the order of metal toxicity in the experimental plant-soil-metal systems used at pH<6.0 followed the order :

$$Cd > Zn > Pb$$

In Fig.5.4.7 reduction in plant height is most prominent at the lower pH's in the Pb, Cd and Zn treatments. However, the most striking feature is the effect that the Cd treatment had upon plant height over most of the pH range. Plant height appears to be a more sensitive indicator towards adverse conditions produced by high levels of Cd in the soil. Another aspect of the sunflower growth is shown by the root: shoot weight ratio in Fig.5.4.8. Attention is drawn towards the Cd treatment ratios and the control ratios which are almost the mirror image of each other about the horizontal axis (about 0.33/0.34 ratio). As to whether this feature is as a result of Cd toxicological impact or a chance artefact is unclear. However, root-to-shoot ratio is a measure of the change in below-ground to above-ground biomass and is a very sensitive indicator of environmental stresses (Hunt 1982, see Chappelka and Chevone 1989).

Fig.5.4.9a-d demonstrates the proportion of metal within the shoot material in relation to the rest of the plant / soil system. Values have been calculated using the entire shoot weight; i.e. the assumption has been made that the small fraction of mass that made up the lower stem cotelydon contained the same mean concentration of metal in it's tissue as the rest of the above-ground mass of the plant. Approximately 260 grams (dry weight) of soil was used per plant pot. The calculations used to obtain the data plotted upon Fig.5.4.9 were the same used to obtain the data for the % efficiency of plant extraction in Fig.5.3.3.

Fig.5.4.9a-d would appear to indicate that the % efficiency of extraction of metals tended to increase with decreasing pH. This was probably the result of increasing metal solubility and bioavailability in all the metal treatments with decreasing pH. However, the % efficiency of extraction was somewhat depressed at the pH3.75 level, probably as a result of greater prevailing toxic conditions. The % efficiency of extraction was worst in plants grown on soils amended with 100 mg/kg Cd. Even the plant shoot % Cd was lowest for the Cd treatment plants, whereas Zn treated and Pb treated soils increased the % efficiency of extraction of Zn and Pb respectively within the plant

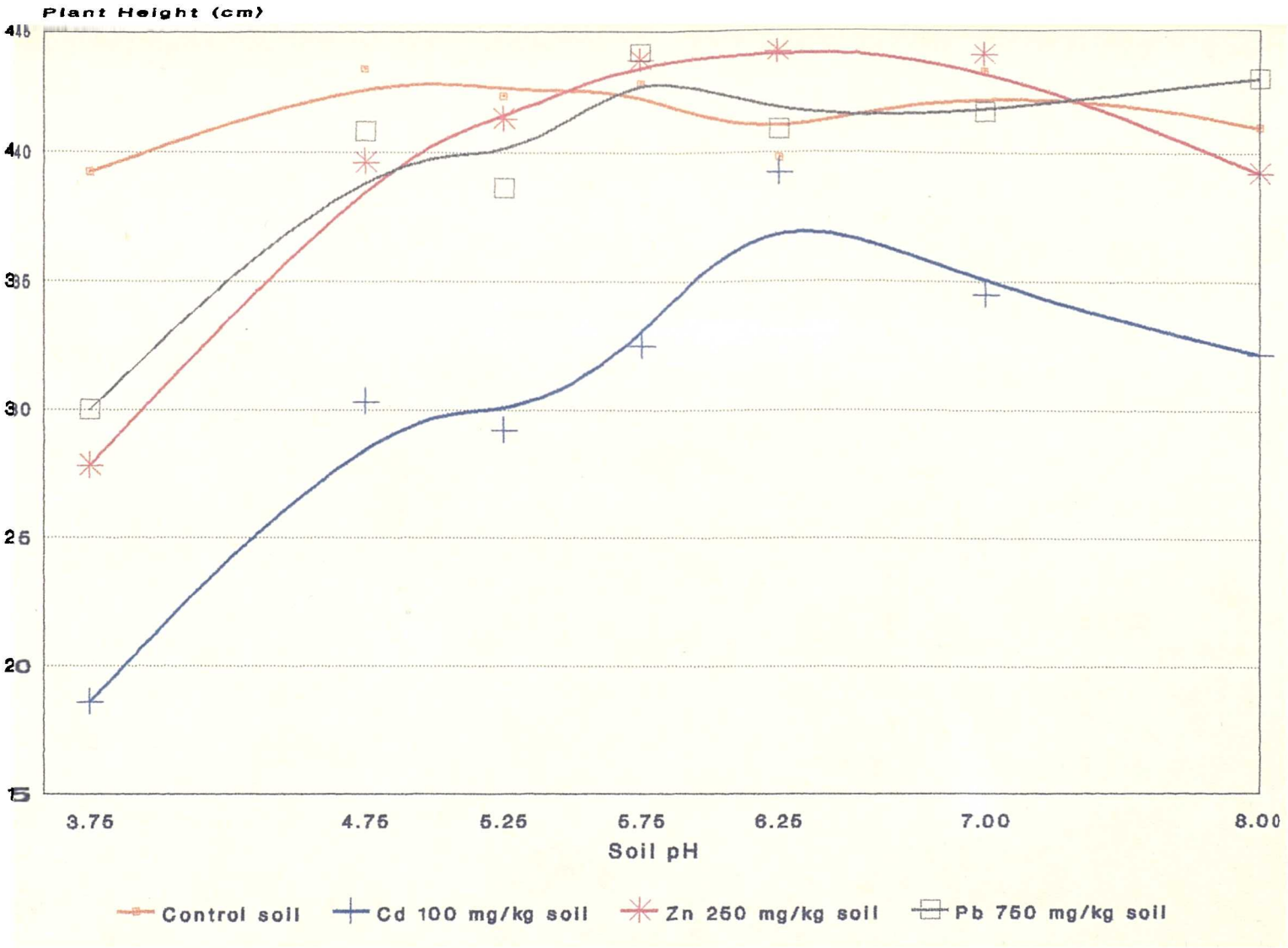


**Fig.5.4.7 Sunflower Height**

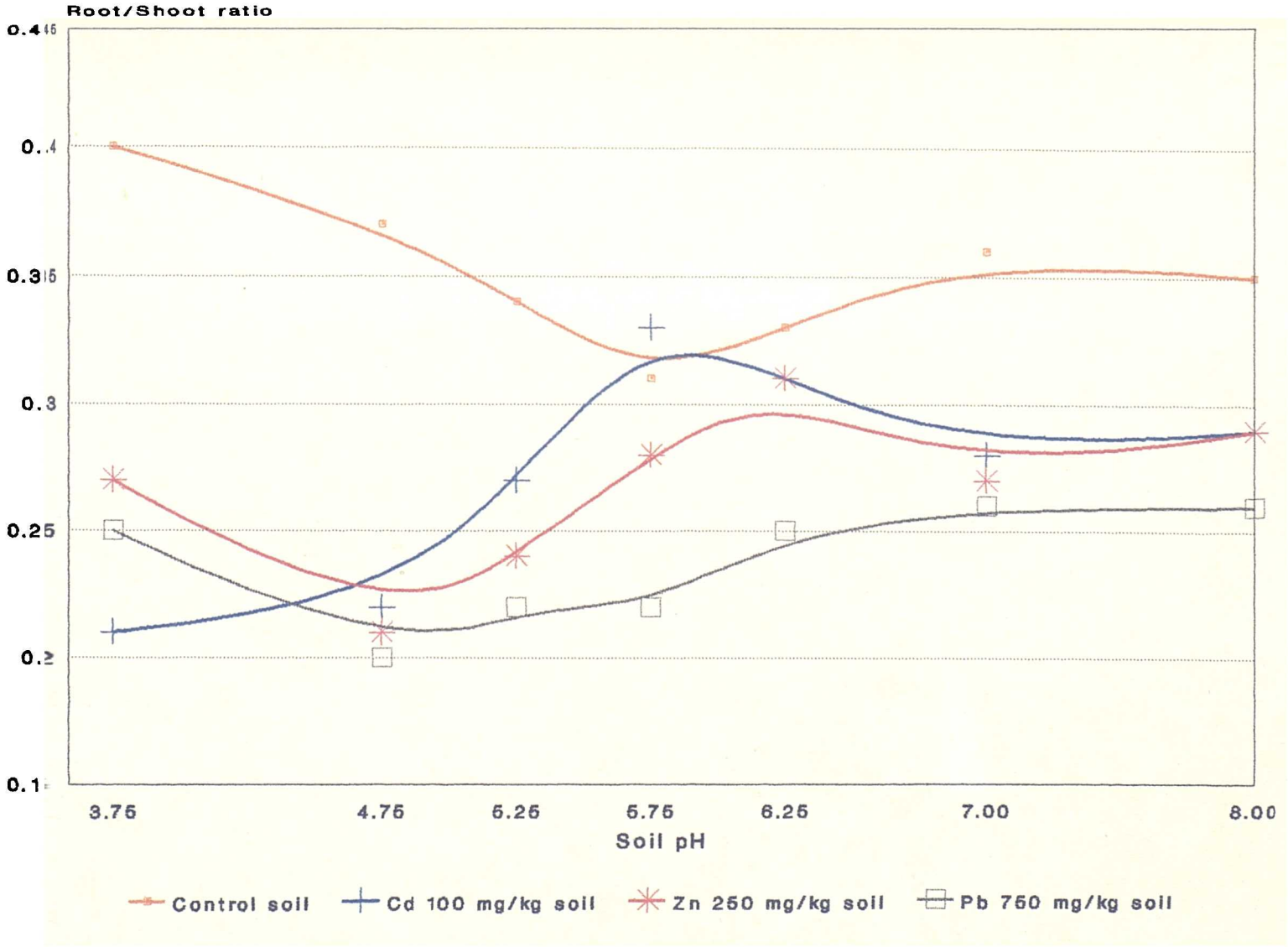


**Fig.5.4.8 Sunflower: Root/Shoot Ratio**

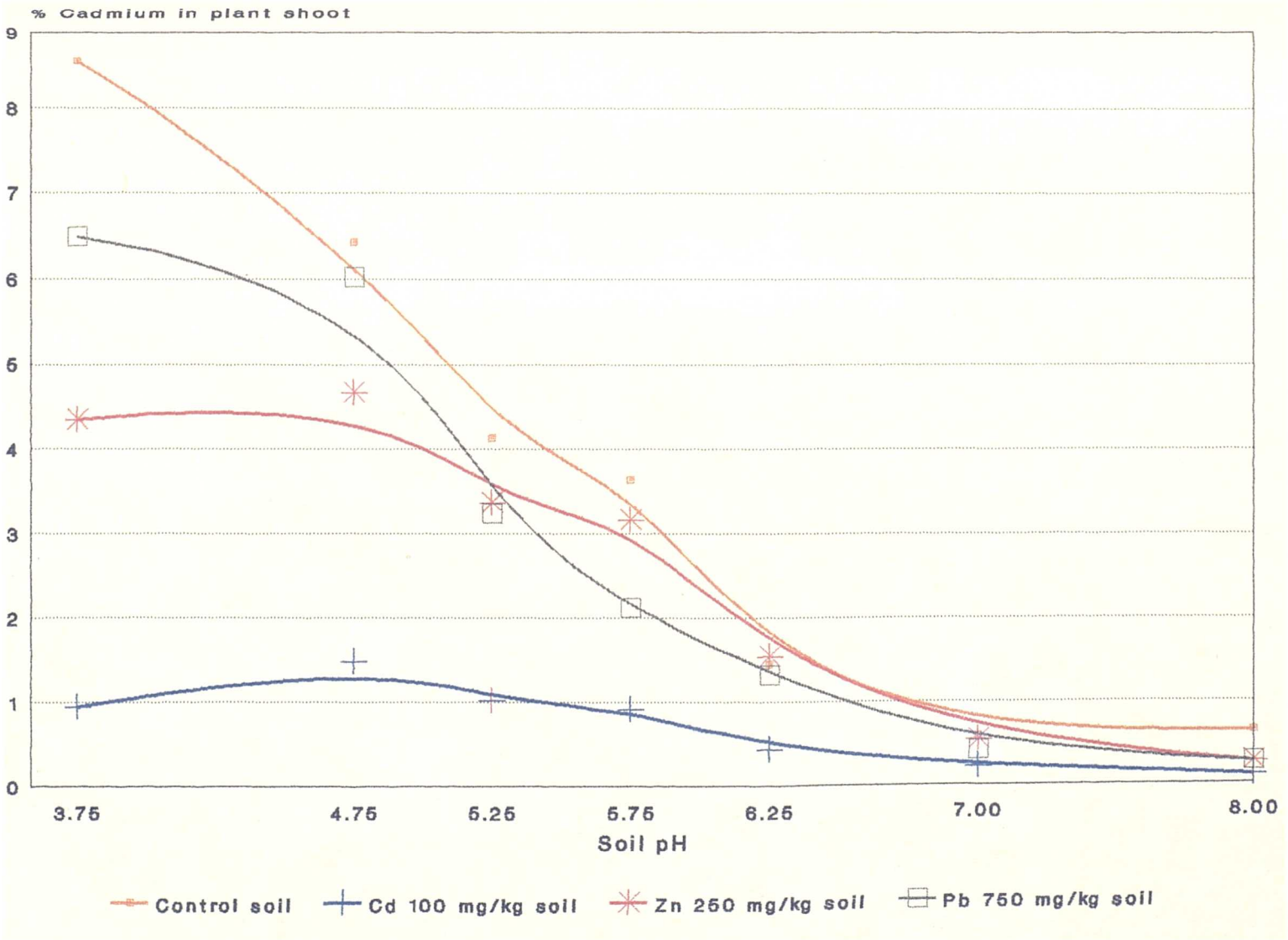


**Fig.5.4.9a Sunflower Cadmium**

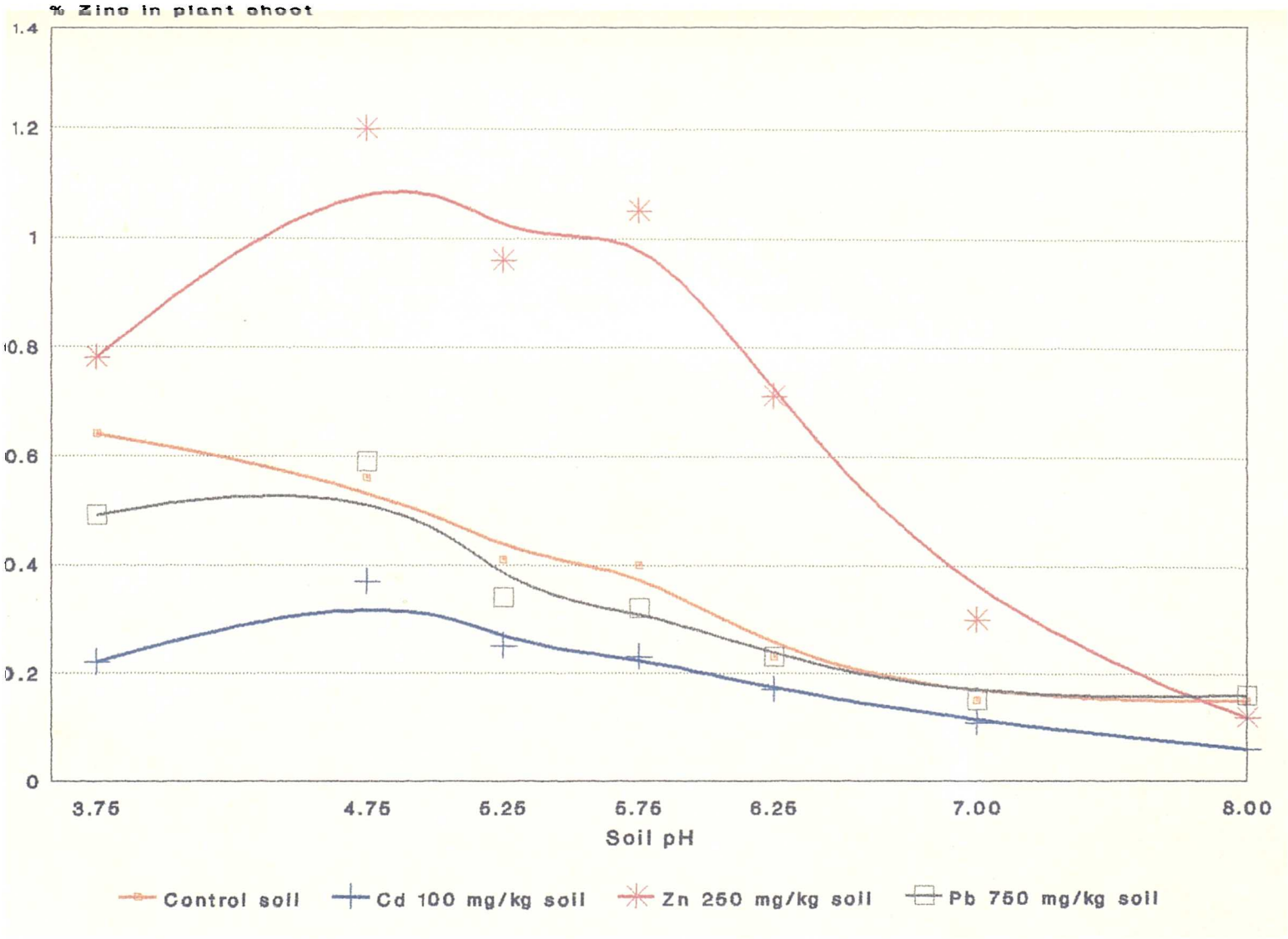


**Fig.5.4.9b Sunflower Zinc**

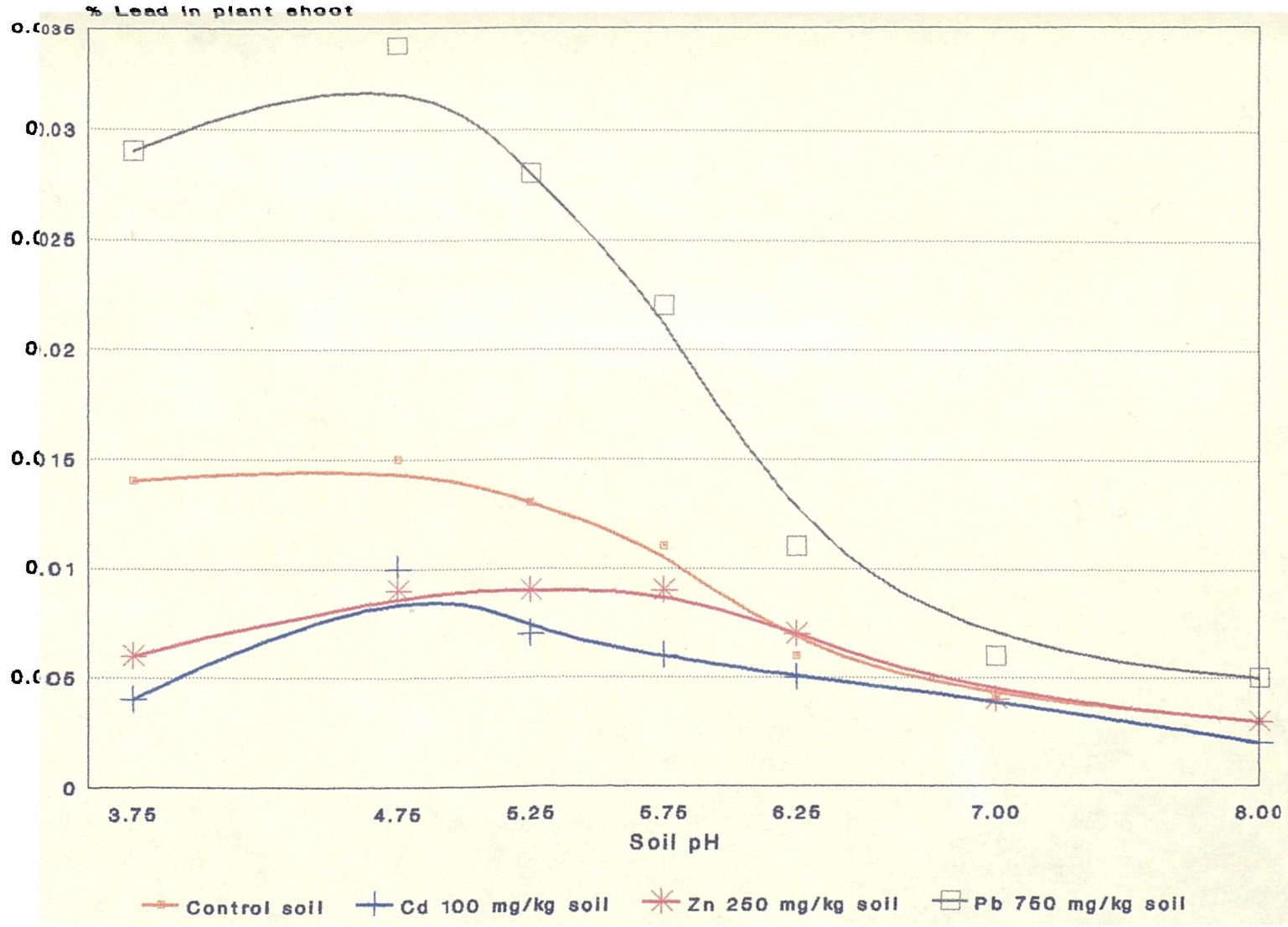


**Fig.5.4.9c Sunflower Lead**

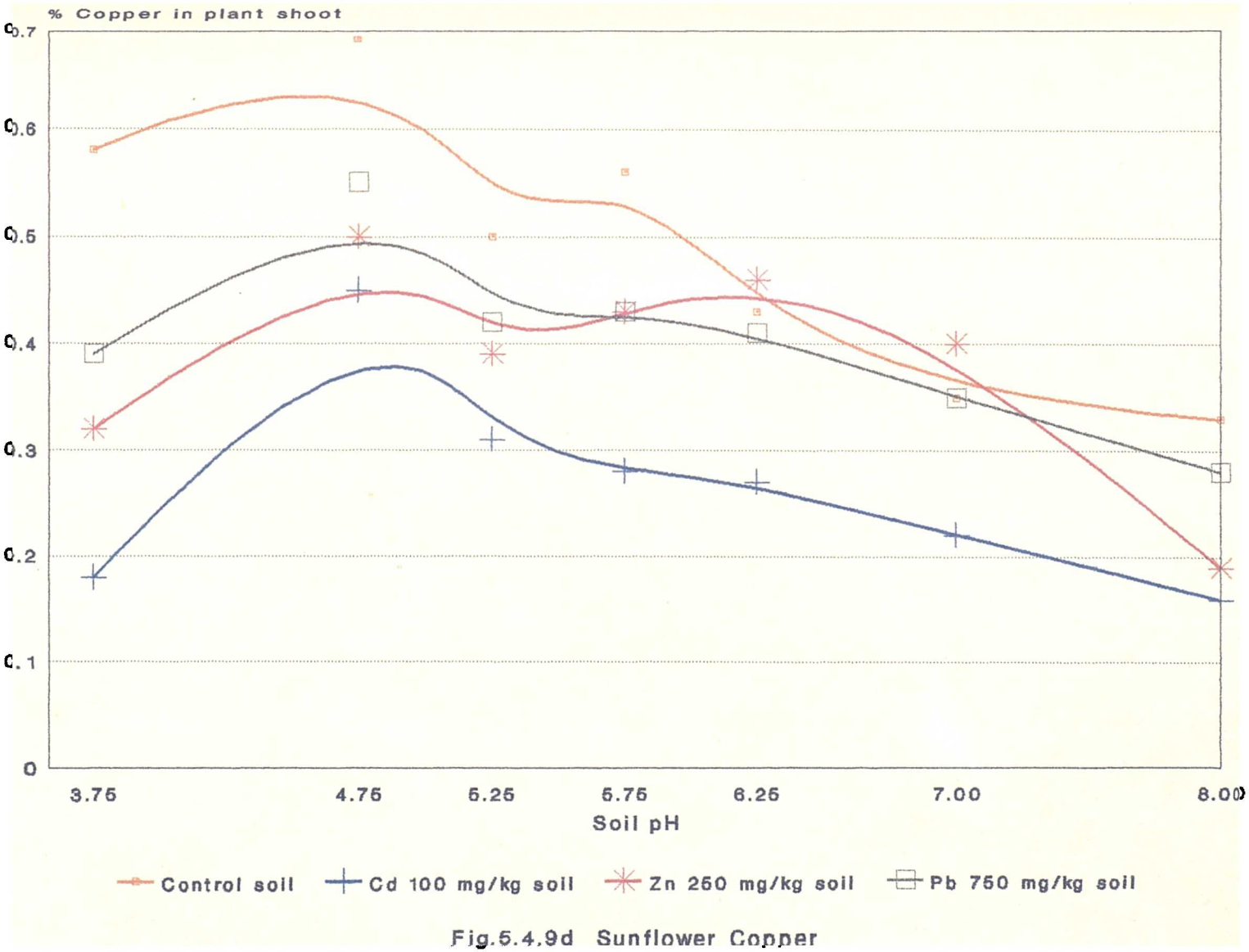


Fig.5.4.9d Sunflower Copper

shoots. This perhaps emphasizes how much more toxic the conditions were for plants grown in the Cd treated soil. Nevertheless, comparison of the percentage of metals taken up between Fig.5.4.9a-d shows that the order of % efficiency of extraction (plant availability) of the metals to uptake into the above ground parts of the sunflower plants was:

$$Cd > Zn \geq Cu > Pb$$

The order shown above resembles those orders described in Section 5.3 for *Holcus lanatus* uptake of these metals from Haw and Hallen soils. Again, the % efficiency of extraction for the two essential micronutrients Zn and Cu were similar; it is possible that plant root organic exudates have encouraged the solubility of Cu with respect to Zn. Xian (1989) and Xian and Shokohifard (1989) also suggested that the uptake rate of Cd, Pb and Zn in the soil followed the order:

$$Cd > Zn > Pb$$

They suggested that such orders should correspond to the degree of solubility of the metals in the soil.

## 5.5. Summary and Conclusions

(a) The availability of a heavy metal in the soil for plant uptake is governed by a variety of conditions related to three primary factors: the plant, the soil (or growth media) in which the plant grows and the heavy metal element. Of the four heavy metals considered (Cd, Cu, Pb and Zn), the general consensus is that Cd is the most bioavailable and phytotoxic.

(b) The general importance in the availability of heavy metals for plant uptake by *Holcus lanatus* grown on Haw and Hallen soil profiles is suggested as following the order:

$$Cd > Zn \geq Cu > Pb$$

The above is similar to the order specified for soil extraction availability of heavy metals in Hallen and Haw soils in Chapter 3, Section 6:

$$Cd > Zn \gg Cu > Pb$$

However, Cu appears to be surprisingly plant available in relation to Zn and the above order of availability is perhaps more closely associated with the % solubility of the metals in the soil solution (see Chapter 4, Section 3) where % solubility decreased:

$$Cd > Zn \geq Cu > Pb$$

(c) The importance of soil acidification on heavy metal uptake by sunflower is illustrated in Section 5.4. Again, plant availability of heavy metals followed the order shown in (b):

$$Cd > Zn \geq Cu > Pb$$

The importance of this section is that it illustrates the primary role of pH in controlling the plant availability of Cd, Cu, Pb and Zn in soils.

# CHAPTER 6

# FINAL DISCUSSION AND CONCLUSIONS

Soils and sediments formed or deposited on the earth's surface can act as vast reservoirs for the containment of heavy metals (such as Cd and Pb); soils are particularly important as they contain surface-active mineral and humic constituents involved in reactions that affect metal retention (Evans 1989). The input into forest floors and forest soils of atmospheric heavy metals such as Cd, Zn and Pb can lead to metal enrichment within those forest components (Banin *et al.* 1987). Even as early as 1882, Francis Phillips recognised that many manufacturing processes gave rise to a "gradual impregnation of the soil" with heavy metal contaminants (Jarvis 1977). More recently the transport of a heavy metal such as Cd through soil profiles into ground water has become a prime environmental concern (Amacher *et al.* 1986).

McGrath (1987) reviewed reports on heavy metal mobility from field experiments of long duration on arable soils treated with sewage sludge. Most of the field experiments lasted for 3-9 years (one example being 13 years in duration) and no metal movement was recorded below soil depths of 30 cm. A greater proportion of the field studies did not report the soil depth to which sludges were incorporated; however, despite this, McGrath (1987) concluded that in the short to medium-term, hardly any leaching of metals below the plough layer occurred over a large range of sludge combinations and soil types. However, Sidle and Kardos (1977) found that in waste water treated soils of a hardwood forest ecosystem small amounts of Cu, Zn and Cd eventually moved out of the 120 cm deep layer of the soil profile, whilst a metal such as Pb showed little penetration down the profile.

It is generally agreed that Cd and Zn are relatively more mobile in soils than heavy metals such as Pb and Cu (Martin and Coughtrey 1987). Hence Mayer (1978) effectively simulated the transport and redistribution of Cd and Pb over a 10 year period. He concluded that the results of the simulation runs were in accordance with the situation in real soils where often strong accumulation of Pb is found in the top soil, while Cd can be redistributed more quickly down soil profiles. The computer modelling study of Martin and Coughtrey (1987) for heavy metal movement in Hallen Wood utilized real field data and hence carried the concept of a simulation model (e.g. such as that used by Mayer 1978) one tangible step forward. The residence times calculated by Martin and Coughtrey suggested that the mobility of the principal heavy metal contaminants

in Hallen Wood follows the order Cd > Zn >> Pb. Further soil profiles taken from Hallen Wood since that study have shown that further movement and redistribution of Cd and Zn to greater soil depths has occurred. The neighbouring site of Haw Wood, however, has not shown the same degree of Cd and Zn redistribution with soil depth over time. Factors such as lower heavy metal burdens of Cd, Zn and Pb, and maintenance of higher soil pH have enabled the latter site to generally maintain distinct concentration gradients of these metals with depth so that the principal contamination has been confined to the surface mineral soil layers.

There are a number of possible explanations that could be put forward to explain the recorded "wave" movement of Cd and Zn down the Hallen soil profiles. Three possible explanations have been considered by Martin and Coughtrey (1987) but have largely been discredited by the authors:

(a) Soil mixing by earthworms: however, in Hallen Wood soils this has been negligible because earthworms of the burrowing type are virtually absent (Hopkin *et al.*1985) and incorporation and redistribution of organic matter has been extremely restricted.

(b) The atmospheric input of heavy metal contaminants within the Hallen Wood system has been sufficiently large enough to create the "wave"-like movement of Cd and Zn. However, atmospheric input within the ecosystem has been considered insufficient. Even during the mid 1970's when smelter emissions were higher and an internally burning smelter waste tip was moved, the input of metals into the site was still insufficient to have created the "wave" movement.

(c) An increased rate of release of metals from litter by enhanced decomposition. However, whilst Zn and Cd have been lost Pb has been observed to be accumulating in the litter layer, and there is no indication that litter decomposition has been enhanced.

Further explanations for the Cd and Zn "wave" formation could be:

(d) Macropore formation caused by the decay of old root systems or pedoturbation processes such as desiccation cracks during times of drought. Such features could undoubtedly encourage throughput of particulates from the highly contaminated organic surficial layers to greater depth. However, such features would only be temporary due to the expanding nature of clays such as montmorillonite. Also incorporation

and redistribution of organic matter within the soils has been extremely restricted (Martin and Coughtrey 1987). Furthermore, it seems likely that if these physical features were the prime cause of the Cd and Zn "wave", it might be expected that a substantial Pb "wave" would also be apparent.

(e) Plant uptake and downward translocation in plant roots (e.g. see Stevenson and Welch 1979). After root absorption, the extent to which heavy metals are translocated to the tops of plants follows the order Cd > Zn > Cu > Pb (Kabata-Pendias and Pendias 1984). As Cd and Zn are more easily mobilized within the plant system with respect to Pb (Balsberg 1989) it might be envisaged that the former elements could be translocated more readily down plant root systems. However, visual inspection of the soil profile (see Table 1.1.4, Chapter 1) suggests that root abundance tends to decrease with soil depth. The soil is also a gley soil (with ferrimanganiferous nodules and mottling features being present) which also suggests that seasonal waterlogging is a feature of these soils; this factor is more likely to restrict the greater proportion of root growth and activity to the upper surface soil.

It would appear that the "wave" like movement of Cd and Zn in Hallen soil with time has principally been encouraged by the relatively greater mobility of these two metals, with respect to the heavy metals Cu and Pb. A factor such as the greater burden of Cd and Zn within Hallen Wood, as opposed to Haw Wood, (see Martin and Coughtrey 1981, Martin *et al.* 1982) in conjunction with the greater acidity of the soil at the former site would help enhance Cd and Zn mobility within the Hallen soil. An assessment of the "availability" and "mobility" of heavy metals is required if informed judgements are to be made about the construction of environmental guide-line limits for potential toxic hazards and about the chemical behaviour and fate of heavy metal contaminants in soil (Gibson and Farmer 1986). The mobility / availability of heavy metals in Hallen and Haw woodland soils followed the order:

$$Cd > Zn > Cu = Pb$$

This order of mobility was based upon data collected by chemical extraction and is in concordance with many other reports which use similar techniques to assess mobility / availability of heavy metals in soils. One report in particular, by Stockart *et al.* (1983), described the mobility of Pb, Zn, Cd, and Cu in highly polluted soils of two contrasting soil types located near Zn smelters in

Belgium. The concentration data they obtained with soil depth showed that there was little movement of metals in the neutral loamy soil, whereas in acidic (pH4) sandy podzolic soils considerable movement of metals occurred. In the latter instance movement of metals was associated with organic matter, with the following series in mobility:

$$Cd > Zn > Cu > Pb$$

Stockart *et al.*'s sites bear some resemblance to the Hallen and Haw Wood sites e.g. in terms of the type of contamination (aerial metal input) and soil pH. The sites also had a range of contamination which encompassed that of Hallen and Haw Wood sites. The movement of heavy metals within the higher pH Belgium loam soil and Haw Wood soil was relatively subdued. However, movement of heavy metals was readily apparent within the lower pH Belgium sandy soil and Hallen Wood soil. The pH of the Hallen Wood top soils were generally comparable to the mid-upper range of the sandy soils, and substantially less than the pH of the loam soils: however, Hallen Wood soils were in texture quite different and are heavy clay soils.

Stockart *et al.* (1983) considered that Cd and Zn became mobile in their soils when the soil pH was $\leq 6$ and pH $\leq 5$ respectively. Martin and Coughtrey (1987) suggested that acidification of the Hallen soil profile to pH values below pH6, to substantial soil depths, has resulted in the observed movement of Cd and Zn. pH data collected from Hallen Wood demonstrates that soil pH from the recent 1987 profile only reached or exceeded pH6 at soil depths of $> 0.5$ metres. Soil Cd and Zn concentrations in the 1987 Hallen profile exceeded upper limit soil background concentrations of 2mg/kg for Cd (Thornton and Plant 1980) and 300mg/kg for Zn (Bowen 1966) at soil depths *circa* $\leq 0.5$ metres. Where soil pHs exceeded pH6 at greater soil depths background concentrations of these metals were to be found. In relation to nearby woodlands on similar soil parent material (Martin and Coughtery 1987) and with respect to similar soil parent material located in surrounding regions and counties, the Hallen Wood soil appears to be uncharacteristically acidic within the top horizons of the soil. Hallen Wood is close to the major nitric acid plants and downwind of a major sulphuric acid plant, and it is believed that acid deposition has been the prime cause of acidification of the soil profile (Martin and Coughtery 1987). Maintenance of an acidic soil pH in the topsoil and a reduction of soil pH at depth would encourage the movement of Cd and Zn down the Hallen profile with time.

It may appear strange that as Hallen soil has become so acidic with time, why should the Haw topsoil also have not reached pH levels of near pH4? Despite the close proximity of the two woodlands to each other, it would appear that Haw Wood is less exposed to the emissions of heavy metals and acidic gaseous emissions from Avonmouth. The Avonmouth smelter and sulphuric acid plant are located closely adjacent to one another. Hence if the burden of heavy metals within Haw Wood (Martin *et al.* 1982) is known to be less than the burden of heavy metals in Hallen Wood (Martin and Coughtery 1981) then it seems plausible that the acid deposition into the former site will also be less. Furthermore, Hallen Wood is located closer to the nitric acid plants in Avonmouth, and geographically Haw Wood is sheltered by the ridge upon which Hallen Wood is located from the nitrous gases emitted by ICI Chemicals.

The enhanced mobility of heavy metals in soils may seriously disturb soil organisms and thereby interfere with organic matter decomposition and nutrient availability to higher plants (Ottar *et al.* 1989). Within the Hallen soil profile there is a quantity and proportion of Cd that is mobile to a considerable soil depth. Total concentrations of up to 3-8mg/kg Cd in soils have been assessed as being phytotoxically excessive to plants (see Kabata-Pendias and Pendias 1984). Levels of extractable (2.5% acetic acid) Cd concentrations of generally > 2.5mg/kg existed in the mineral soil between 0-13.5cm depth, and between 13.5-33.5cm depth extractable Cd exceeded 3mg/kg. Cd is considered to be more phytotoxic than Zn, Cu, and Pb, and from bioassay tests using *Holcus lanatus* it would appear that Cd was the most biologically available metal, in relation to the other three elements, within Haw and Hallen soils. Results of the sunflower experiment indicated that acidification of contaminated soil encourages uptake of heavy metals by plants. Different plant species will root down to different soil depths. Hence heavy metal accumulation within a particular horizon of the soil, heavy metal bioavailability within that horizon, and the prospect of future acidification within that horizon will affect plant uptake of these metals and their eventual redistribution within a wider part of the terrestrial environment.

Further continued acidification of Hallen soil will help maintain and encourage soluble levels of heavy metals within the soil solution. In terms of total heavy metal concentrations within the Hallen soil, Cd appeared to be the most readily soluble metal. A high proportion of the solublized Cd in Hallen soil solution occurred as a cationic species of which the free $Cd^{2+}$ form was likely to be of great significance. Much evidence indicates that the uptake of Cd to plants may be related to one of its chemical forms rather than its total

concentration in solution, with free $Cd^{2+}$ probably being the most available form to plants (Hirsch and Banin 1990).

In contrast to Cd, a greater proportion of the burden of Pb has been maintained within the organic litter layers especially at Hallen Wood. The movement and redistribution of Pb down the Haw or Hallen profile was not readily apparent. Despite the level of aerial input of Pb being thirty times as great as that of Cd within Hallen Wood, Pb concentrations below the first few centimetres of surficial soil have been quite normal, whereas there has been substantial Cd contamination of soil to depth. In relation to Cd, Pb was relatively immobile and non-bioavailable in Haw and Hallen soils. However, continued acidification of the Hallen topsoil and the maintenance of soil pH values of < pH4 for prolonged periods of time may see considerable movement of Pb into the Hallen topsoil considering that there is a vast reservoir of Pb retained within the woodland floor. Increased movement of Pb down the Hallen profile is likely to expose plant roots to increased levels of bioavailable Pb. In conjunction with this scenario increased acidity stress would also bring about other manifest problems such as the further depletion of Ca and Mg, and the enhancement of mobile / available Al.

Straughan *et al.* (1981) suggested that the significance of heavy metal mobilization as a result of acid deposition stemmed from the fact that not only were the metals mobilized from surface mineral and organic layers of soil, but also readsorption in subsurface layers was reduced (hence metals became available for subsurface leaching). They stated that heavy metals deposited on vegetation from atmospheric sources were mobilized by acid deposition, such that under these conditions retention of heavy metals by vegetation, soil components and organic matter was altered and the rate of their removal was increased giving rise to potential impacts on water and soil quality. With respect to Hallen soil, the rates at which mobile forms of heavy metals are removed from the rooting zones of the species within the woodland biomass, and the rate of entry to water courses, and hence availability to other systems, are important considerations especially in the case Cd (Martin and Coughtery 1987). In the instance of the Haw soil, the rate of movement of heavy metals further into the rooting zone with time is perhaps the prime consideration. Total concentrations of up to 400 mg/kg Zn in soils have been considered as being phytotoxically excessive (Kabata-Pendias and Pendias 1984). Concentrations of Zn in excess of 400 mg/kg Zn have already been recorded in the Hallen soil moving with time from the surficial layers to depth. If further movement of metals down the Haw soil profile is to be relatively restricted / more long term

in relation to the Hallen soil profile, then the opportunity for excessive concentrations of heavy metals to build up with time in the topsoil / rooting zone seems inevitable.

As there appears not to be as great an input of heavy metals and acid deposition within Haw Wood in relation to Hallen Wood, it might be expected that a lag time between heavy metal profile development in the Haw soil and heavy metal profile development in the Hallen soil is inevitable. However, the manner in which future movement of metals, such as Cd and Zn, occurs down the Haw profile may well be different to that which has been shown to occur in the Hallen soil. The evolution of the "wave"-like movement of Cd and Zn down the Hallen soil profiles may be a feature peculiar to this site.

In summary, Hallen and Haw Woods, despite sharing similar ecological and pedological characteristics, have been shown in the course of being aerially contaminated by heavy metals, to have developed dissimilar soil profile characteristics with time, in terms of the distribution of Cd, Cu, Zn and Pb with soil depth. This may be partially due to the Hallen site having a greater burden of heavy metals deposited upon it. But the movement of a Cd and Zn "wave" down the Hallen soil profile with time appears to have been encouraged by the uncharacteristically low levels of pH that have prevailed within the topsoil. The Maintenance of soil pH below pH6 at depth has allowed Cd and Zn movement to proceed to deeper soil horizons that have previously maintained background concentrations of these metals within the Hallen soil. Acid deposition is believed to be the major cause of acidification of the Hallen soil profile and it has been suggested that progressive acidification of to pH values below 6 to substantial soil depths has resulted in the observed movement of Cd and Zn. The low percentage base saturation figures recorded in the topsoil of the latest Hallen 1987 profile and the recording of soil pH at < pH6 to a depth of 0.5 metres in the same profile have encouraged Cd and Zn contamination to depths of at least 50±3cm depth.

However in Haw Wood soil the pH levels were quite normal and characteristic of the soil type. Most of the heavy metal contamination was restricted to the top 10-15 cm of soil. Unlike the Hallen soil profile, there was no major redistribution or movement of Cd and Zn down the Haw profile with time. The relative distributions of Cu in the Haw and Hallen soil profiles were remarkably similar and no major redistribution of this metal occurred with time. Despite the higher levels of aerial input of Pb into the woodland systems (with respect to Cu) there was no major redistribution and movement of this element down the soil profiles with time. Soil Cu concentrations in Haw and Hallen

soil occurred well within concentration ranges defined as background soil concentrations. Pb contamination was confined to the top surficial layers of soil - most of the soil Pb concentrations being quite normal for soils located close to an urban area. Substantial heavy metal contamination has occurred within the woodland floor (L, F, H layers) of both Hallen and Haw. Concentrations of Cd, Cu, Pb and Zn within the woodland floor exceeded normal / background concentrations of heavy metals for woodland litter layers. A considerable proportion of the Pb burden occurred within the woodland floor especially within the latest Hallen profile.

Sequential chemical extraction of heavy metals in Haw and Hallen soils demonstrated that the relative mobility / bioavailability of the metals followed the order:

$$Cd > Zn > Cu, Pb$$

However, due to the similar proportionation that Cd and Zn both shared in their non-residual extracted forms and Zn being quantitatively much more abundant within its mobile forms, helps to explain how the Zn "wave" moves in comparative unison with the Cd "wave" with time in the Hallen Wood soil.

Proportionally, the heavy metals in the Hallen soil were more mobile / bioavailable than they were in the Haw soil. Generally, within the Hallen mineral soil, > 50% of the Cd was "available" (non-residual) to 51cm depth. The relative solubility of heavy metals within the Hallen soil followed the order:

$$Cd > Zn > Cu > Pb$$

The greater proportion of Cd and Zn within the Hallen soil solution occurred as cationic species. Within the Haw topsoil (0-11cm) the relative solubility of all four metals was diminished with respect to the degree of solubility expressed by metals within Hallen Wood topsoil. Zn appeared to be relatively more soluble than Cd within the Haw topsoil, but both metals were still principally dominated by cationic species in solution. Soluble Cu appeared to be mainly associated with organo-complexes (low polar organics and/or anionic species) in both Haw and Hallen soil solutions. However the speciation of soluble Pb seemed to depend largely upon prevailing soil conditions.

Results from the bioassay test using Hallen and Haw soil and from the sunflower pot experiment seemed to suggest that the relative availability of the heavy metals for plant uptake over the range of conditions followed the order:

Cd > Zn > Cu > Pb

Of the four heavy metals considered in Haw and Hallen soil, Cd would appear to be the most mobile and bioavailable metal in relation to its total concentration in the soil. High levels of Cd contamination existed in the surficial soil layers of Haw and Hallen Wood; hence the greater mobility / bioavailability of this metal in the soils pertains particular importance with respect to its eventual fate as Cd is toxicologically of great concern with respect to, amongst other things, human health. In contrast Pb was relatively immobile and biologically unavailable with respect to its total concentration within the two soils. In some respects the relative mobility / availability of Zn was not as great as might be expected, especially when it is considered that Zn moved concomitantly down the Haw and Hallen soil profiles with Cd. It might also have been expected that the relative availability of Zn for plant uptake would have been much greater in relation to Cu. However, Zn was far more abundant than Cd, Cu and Pb in quantitative (concentration) terms with respect to its available forms. Hence the movement of Zn down the Hallen profile with time was very apparent, and the potential biological impact that Zn contamination within the Hallen and Haw soils might have should not be overlooked.

Overall, this long-term project has shown the movement of heavy metals down soil profiles with time under natural field conditions. The initial input of metals has been principally of an aerial particulate form. Most of the other long-term studies of metal movement (the majority not being of the duration of 8-12 years as at Haw and Hallen Woods) utilize sewage sludge / slurry or waste water as their metal supply; and a number of these studies physically incorporate the sludge within the topsoil. The full biological implications in terms of heavy metal movement down the soil profiles and their respective solid / solution phase requires further attention. Also the presence of acid deposition within the field study area is a factor to be considered. For example, in Hallen Wood, further acidification of the soil at depth would encourage further Cd and Zn movement down the soil, whilst further acidification of the topsoil could eventually start to see Pb move down the soil profile. Considering that the Hallen soil is a heavy clay soil, the recorded extent of movement and soil contamination by Cd and Zn is a rather unusual and unexpected phenomenon.

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References refering to the development of various analytical techniques (e.g. Muller 1930, Parker 1921, Schollenberger 1927, Walsh 1955, Williams 1928) are referred to in Adams *et al.*(1980), Allen (1989), Knight *et al.*(unknown) and Van Loon (1985).

# APPENDICES

{Sources of information for the compilation of Appendix A and B included: Dymott 1985, Knight *et al.*(unknown), Milner and Whiteside 1984, Van Loon 1985 and Pye Unicam HPLC Applications Number 8.}

# APPENDIX A

# TRACE ELEMENT ANALYSIS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

## 1. Introduction

### 1.1. AAS - Its Place in Analytical History

Gravimetric and titrimetric methods were first employed for trace element analysis. More practical and accurate trace element analysis became possible with the advent of instrumentation:

(a) 1930's optical emission spectrometric methods (use of flames, furnaces, arcs and sparks for atomisation-excitation sources) were employed; also colorimetric-molecular-spectrophoto-metric methods were introduced (including nephelometry, turbidimetry and molecular fluorometry).
(b) Late 1930's and early 1940's electrochemical methods were introduced (polarography and anodic stripping voltammetry most widely used).
(c) Early 1960's saw the introduction of atomic absorption spectrophotometry (AAS). This development and the use of modern neutron activation (and other related methods) meant that trace element analysis became a fast developing science.
(d) Late 1970's, the arrival of plasma atomiser-excitation sources for use with optical emission and mass spectrometric methods.

The majority of trace element analyses carried out to this day are done by techniques of valence electron atomic spectrometry with atomic absorption responsible for the largest fraction of the work. Use of inductively coupled plasma (ICP) in conjunction with emission spectrometry is growing fast and in numerous applications will probably come to replace flame AAS. Furnace atomic absorption still attains the best detection limits, and hence this technique should still be widely used by the end of the century (see Table 1.1 and 1.2). Other techniques that are used include X-ray fluorescence, polarography and anodic stripping voltammetry (Table 1.3). For details about sensitivity, detection limits, precision and accuracy see Section 5.

**Table 1.1 Detection Limits in ng/ml for Flame AAS and ET-AAS (Welz 1985)**

| Element | Flame-AAS | ET-AAS |
|---|---|---|
| Cd | 0.5 | 0.003 |
| Cu | 1 | 0.02 |
| Pb | 10 | 0.05 |
| Zn | 1 | 0.001 |

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**Table 1.3 Instrumental Analytical Methods (Hewitt and Harrison 1986)**

| Method | Sample (a) | Specificity | Sensitivity (b) |
|---|---|---|---|
| Gravimetric | SLG | good | >1μg |
| Titrimetric | SLG | good | $>10^{-7}$M in soln. |
| Visible spectroscopy | SL | fair | >0.005 ppm in soln. |
| U.V. spectroscopy | SLG | fair | >0.005 ppm in soln. |
| Flame emission spectroscopy | SL | good | >0.001 ppm in soln. |
| Atomic absorption spectroscopy | SL | excellent | >0.001 ppm in soln. |
| Gas chromatography | LG | excellent | >10 ppm |
| Liquid chromatography | SL | good | >0.001 ppm |
| Polarography | L | good | >0.1 ppm |
| Anodic stripping voltammetry | L | good | >0.001 ppm |
| Spectrofluorometry | SL | good | >0.001 ppm |
| Emission spectroscopy | SL | excellent | >0.1 ppm |
| X-ray fluorescence | SL | good | >10 ppm |
| Neutron activation | SL | excellent | >0.001 ppm |
| Mass spectrometry | SLG | good | >0.003 ppm |

(a) S=solid, L=liquid, G=gas
(b) Approximate only, depending upon the particular element being analysed.

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**Table 1.2 Sensitivities and Detection Limits of Analytical Techniques**

| Element | ASV[a] Detection Limits (ppb) | Flame AAS[b] Detection Limits (ppb) | ET-AAS[c] Detection Limits (ppb) | ICP-ES[d] Detection Limits (ppb) | NAA[e] Sensitivity (ppb) |
|---|---|---|---|---|---|
| Cd | 0.005 | 1 | 0.003 | 1 | 5 |
| Cu | 0.5 | 2 | 0.4 | 2 | 2 |
| Pb | 0.01 | 10 | 0.05 | 20 | 500 |
| Zn | 0.4 | 0.6 | 0.2 | 1 | 100 |

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# 2. AAS - Techniques and Instrumentation

## 2.1. Principles of an Atomic Absorption Spectrophotometer

The first analytical application of atomic-absorption was by Müller (1930). The general usefulness of the method was not readily appreciated until the mid 1950's (Walsh 1955). Between 1955 and 1962 there was little useful commercial instrumentation available. Some of the earlier equipment produced for routine work by Walsh and his co-workers bear remarkable similarity in principle to modern atomic absorption units. The basic layout of an atomic absorption system is shown in Fig.2.1.

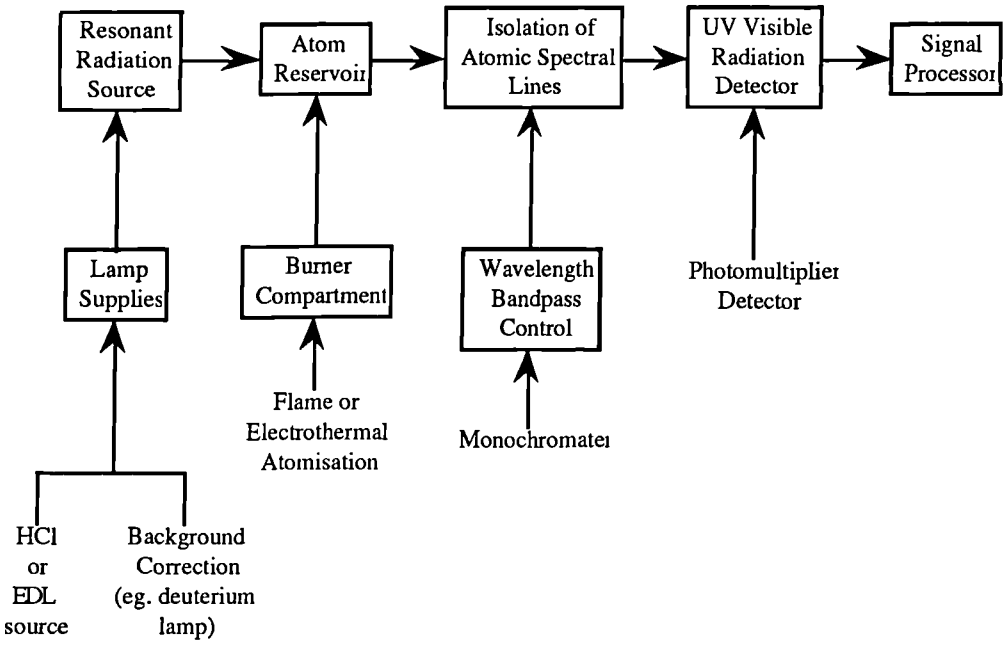


Fig.2.1 Block layout of an atomic absorption spectrophotometer (path of lightbeam crosses from left to right i.e. from the resonant radiation source to the signal processor).

Atomic absorption is a physical process involving the absorption, by free atoms of an element, of light at a wavelength specific to that element. Metallic and non-metallic elements have valence electrons which are relatively loosely bound to their nucleus and which can be excited by photons of wavelengths in the 190-900nm range. For each atom of a metal, the energy gap between ground state level and the first energy level for a particular valence electron is nearly identical, and this energy gap is not found exactly in any other element. Therefore, only one specific element will absorb photons of light at a specific wavelength. Radiation of a characteristic wavelength is produced by a hollow-cathode (HCL) or electrodeless discharge lamp (EDL). The flame or furnace atomisers produce free atoms from the introduced sample (aided by spray formation from a nebuliser glass bead head in the case of flame AAS). The desired wavelength of the element in question is then isolated from other absorbing or non-absorbing lines of radiation. The detector is usually a photomultiplier tube.

Absorbance is often the quantity measured by an AAS:

$$A = \log \frac{I_o}{I} = KCL$$

where A = absorbance, $I_o$ = intensity of incident beam, I = intensity of the transmitted beam, K = absorption coefficient, C = concentration of absorbing atoms and L = path length of the optical beam. A near linear relationship exists between absorbence and the concentration of the considered element within an optimum working range from the detection limit. At the higher absorbance levels, curvature in the relationship occurs. Curvature within the linear relationship is a result of residual or stray light (see Fig.2.2). The trace elements most easily determined by atomic absorption include Cd, Cu, Pb and Zn.

## 2.2. The Hollow-Cathode Lamp : Radiation Source

The lamps are filled with inert argon or neon gas. Within the lamp a high voltage is passed between an anode and a cathode (the latter is made up of the analyte element) which causes ionisation of the gas creating positive ions which bombard the cathode. This in turn causes release of the analyte element from the cathode. Ejection of the analyte atoms and their excitation produces a release of electrons, thus creating emission. Hollow cathode lamps for Pb are

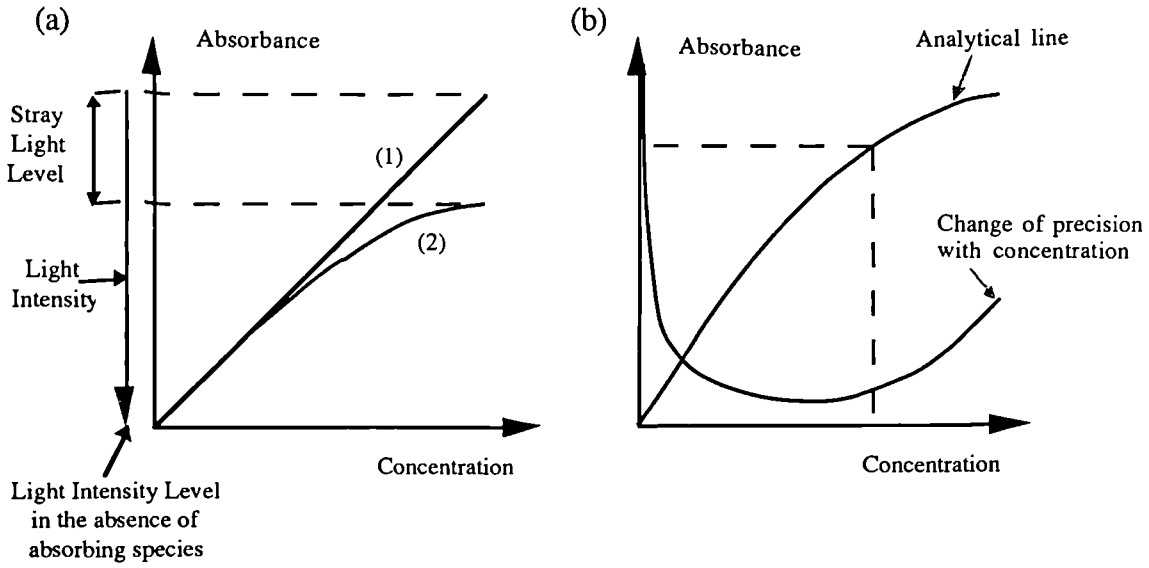


Figure 2.2 (a) Linear and curved calibration curves
(1) For a determination with little or no stray light present
(2) For a determination where there is a significant stray light signal

(b) Change of precision with concentration absorbance

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far less satisfactory than are lamps for Cd, Cu and Zn. The lifetime of a lamp depends on not only on the loss of analyte metal from the cathode (redeposited elsewhere on the lamp), but also leakage of ambient gases into the lamp.

## 2.3. Flame Atomisers

Flame AAS provides better precision than ET-AAS. Detection limits depend upon the matrix solution. There are three available flame types: air-propane, nitrous oxide-acetylene, and air-acetylene. The air-acetylene flame is perhaps the most commonly used and this provides the best sensitivity for Cd, Cu, Pb and Zn (Table 2.1).

Flame atomisation may succumb to any of the following interferences:

(a) Atomic spectral interferences - negligible as a result of the simplicity of the absorption spectra and narrow line emission from radiation lamp sources.
(b) Physical interferences - due to aspirated solutions of different viscosities e.g. non-acidified standard solutions have low viscosities, whereas highly acid sample solutions result from sample acid digestion; therefore standards should be prepared with similar acid contents to the samples.

**Table 2.1 Elemental Performance Data (from Milner and Whiteside 1984)**

| Element | Wavelength (nm) | Buffer | Flame | Sensitivity ($mgl^{-1}$) | % Precision at 0.5A | Bandpass (nm) | Lamp Current (mA) |
|---|---|---|---|---|---|---|---|
| Cd | 228.2 | - | Air/Acetylene | 0.010 | 0.35 | 0.4-0.5 | 3-6 |
| Cu | 324.8 | - | Air/Acetylene | 0.035 | 0.25 | 0.2-0.5 | 2-5 |
| Pb | 217.0 | - | Air/Acetylene | 0.10 | 0.35 | 0.4-0.5 | 3-6 |
| Zn | 213.9 | - | Air/Acetylene | 0.01 | 0.35 | 0.2-0.5 | 4-10 |

## Table 2.2 Elements: Flame Type and Interferences (from Van Loon 1985)

| Element | Flame Type | Comments |
|---|---|---|
| Cd | A, L | Cationic interferences slight |
| Cu | A, L | Cationic interferences minimal |
| Pb | A, L | Cationic interferences minimal. Avoid $SO_4$ |
| Zn | A, L | Cationic interferences minimal |

A = Air-acetylene L = Lean

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(c) Ionisation interferences - elements such as Na, K, Rb and Cs ionise very easily. To ensure the same degree of ionisation between standards and samples, an ionisation buffer should be used e.g. for K determinations standards and samples are made up to 1000µg/ml Cs.

(d) Chemical interference - failure to completely dissociate compounds of elements in a flame (especially in air-acetylene or lower temperature flames) e.g. a significant fraction of calcium can remain bound as a phosphate at air-acetylene flame temperatures. A releasing agent can be employed at about 1% to sample and standards such as 5000µg/ml Sr.

(e) Background interference - most significant with work near detection limit. Otherwise the problem is minimal in flame AAS.

(f) Non-specific interferences - e.g. molecular absorption and/or scatter less of a problem in flame AAS.

Element interferences and best choice of flame are given in Table 2.2 below.

When working near the detection limit, background correction can help improve levels of detection eg. for Zn the detection limit improves from 0.001µg/ml to 0.0005µg/ml. Nebulisation is also important. Performance can be improved by the use of slotted quartz tubes (STAT - the Slotted Tube Atom Trap) - see Table 2.3. A more recent Varian version is called ACT-80.

These can improve sensitivity of some elements by 2-5 times. More volatile elements such as Cd, Cu, Pb and Zn can benefit from such amendments to the system.

**Table 2.3 Performance Figures Obtained with the STAT (from Milner and Whiteside 1984)**

| | | Slotted Tube | | Conventional | |
|---|---|---|---|---|---|
| Element | Flame Type | Sensitivity | Detection Limit | Sensitivity | Detection Limit |
| Cd | Air/$C_2H_2$ | 0.004 | 0.0005 | 0.010 | 0.001 |
| Cu | Air/$C_2H_2$ | 0.015 | 0.001 | 0.035 | 0.002 |
| Pb | Air/$C_2H_2$ | 0.03 | 0.0035 | 0.100 | 0.005 |
| Zn | Air/$C_2H_2$ | 0.004 | 0.0004 | 0.010 | 0.0008 |

---

## 2.4. Electro-Thermal Atomisers

This involves introducing a 10 to 100µl fraction of sample solution into a graphite tube furnace, which is then subjected to a series of stepwise temperature increases. This enables the analyte element to be freed from the engaging solution matrix so that atomisation of the former occurs. The resulting absorbence signal has height (or area) proportional to the absolute mass of the analyte. Inert gas such as high purity argon or nitrogen is purged into the system on firing to expel any atmospheric oxygen present that could react with the hot graphite tube or sample material. Pyrolytically coated graphite tubes are usually employed to provide optimum performance, ensuring that carbide formation with other elements is avoided. The temperature profile used is also important depending on the complexity of the sample (see Fig.2.3). The recommended ash and atomisation temperatures for the Varian GTA-95 atomiser (the model used in this thesis) are shown in Table 2.4.

**Table 2.4 Recommended Ash and Atomisation Temperatures for the Varian GTA-95 Atomiser**

| Element | Lamp Current (mA) | Wave-length (nm) | Slit Width (nm) | Max. Ash Temp. °C | Atomisation Temp. °C | Sensitivity x$10^{-12}$g |
|---|---|---|---|---|---|---|
| Cd | 4 | 228.8 | 0.5 | 300 | 1800 | 0.3 |
| Cu | 4 | 324.8 | 0.5 | 900 | 2300 | 2.5 |
| Pb | 5 | 217.0 | 1.0 | 400 | 2000 | 3.0 |
| | 5 | 283.3 | 0.2 | 400 | 2000 | 6.0 |
| Zn | 5 | 213.9 | 1.0 | 400 | 1900 | 0.25 |

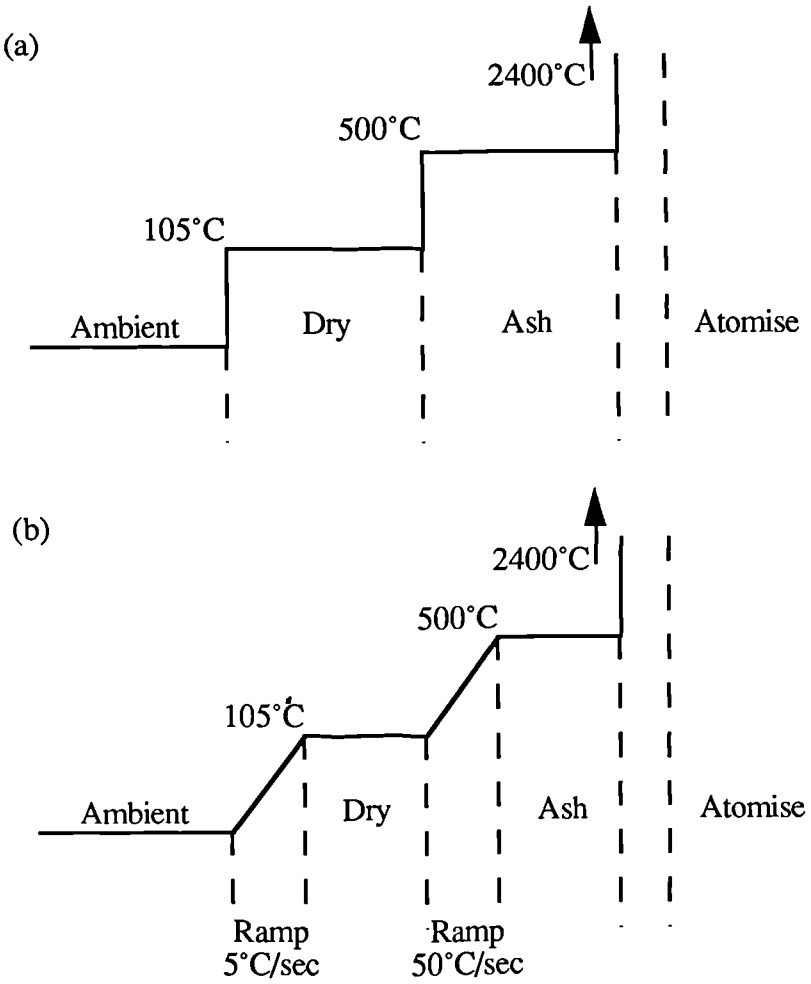


Figure 2.3 (a) Isothermal heating temperature profile
(b) Ramp heating temperature profile - complex samples e.g. those with a large organic matrix

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L'vov platforms are a useful aid to producing isothermal atomisation (a method by which the platform temperature profile lags behind that of the graphite tube wall).

Background correction is very important in electrothermal work. Zeeman background correction is best, but most instruments are equipped with deuterium arc background correction. The detection limits of furnaces are generally far better than those for flame atomisation, but the detection limits by the former method are very much more matrix dependent. Physical and chemical characteristics of the standard and sample matrix can produce interferences. These interferences can be quite complex but may be minimised by the use of a L'vov platform and/or use of standard additions:

(a) Differing Viscosity Interferences - the different viscosities of standards and samples can produce a significant source of error. Standard conditions can help overcome this problem.

(b) Interference from different rates of volatilisation - this is from the coexisting cations and anions in the sample solution. Reagent addition or selective volatilisation of the matrix components prior to atomisation can help. Signal integration or standard addition may also be employed. For standard addition to work, the added analyte should have the same chemical form in the sample as the sample analyte. Standard addition also requires the calibration graph to be linear over the concentration range utilised (calibration graphs have very short linear regions in electrochemical work). Standard addition is also time consuming, but is nevertheless a very useful technique. Elements such as zinc, cadmium and lead can become volatile at relatively low temperatures, especially in their chloride form. Conversion to less volatile nitrate or sulphate forms allays the problem and prevents the analyte from vaporising prior to the matrix.

(c) Background interference - most commercial atomic absorption units cannot correct for background when the interference produces a signal greater that an absorbence of one. Zeeman background correction is useful above this value.

**Table 2.5 Ash Temperature with Wall Atomisation (after Voth-Beach and Shrader 1987)**

| Element | Recommended Ash Temperature (°C) | Ash Temperature With Pb Modifier (°C) | Change (°C) |
|---|---|---|---|
| Cd | 300 | 550 | +250 |
| Cu | 900 | 1100 | +200 |
| Pb | 400 | 1000 | +600 |
| Zn | 400 | 900 | +500 |

(d) Non-specific interferences - matrix modification and/or background correction used. NaCl and organic materials (e.g. in sea water samples, body fluids etc.) can vaporise at relatively low temperatures, which in turn can interfere with the determination of Cd, Pb and Zn (low boiling point elements). Modification of samples (high in chloride) with $NH_4NO_3$ helps to reduce the chloride interference. However, a modifier such as $NH_4NO_3$ can also degrade tube conditions and element sensitivity; but modifying the samples with nitric acid can also effectively reduce halide interference. Use of standard additions is not applicable to overcoming non-specific interferences. The use of a reduced-palladium matrix modifier means that chloride and organic interferences can be greatly reduced, enabling excellent wall atomisation performance to occur (see Table 2.5).

**Table 3.1. Lead in Water, Sludge and Sediment (Loescher 1975)**

| Samples | Water[a] µg/l 1 | 2 | 3 | Sludge µg/g | Sediment µg/g 1 | 2 |
|---|---|---|---|---|---|---|
| Mean of Labs | 6 | 4 | 334 | 1690 | 14 | 14 |
| Standard Dev | 4 | 3 | 56 | 120 | 5 | 6 |
| Range | 2-130 | 2-170 | 280-490 | 1-2500[b] | 5-20 | 4-25 |

a : Water 1 and 2 are splits of the same sample
b : One lab uses $H_2SO_4$ thus precipitating most Pb

Loescher B. 1975. Report to participants in the Toronto Pb Inter-comparison Study. 20pp. In Van Loon 1985

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# 3. Standard Reference Materials and Contamination

## 3.1. Standard Reference Materials

These are vitally important for accuracy assurance in trace metal analysis. Certified values of various elements have been given for numerous materials as a result of analyses carried out in several laboratories using a number of different methods. Some of the supplying agencies include:

(a) National Bureau of Standards, Washington D.C. 20234.
(b) The National Institute for Environmental Studies, Yatake-Machi, P.O. Yatabe, Tsukuba, Ibaraki 300-21, Japan.
(c) International Atomic Energy Agency, Vienna, Austria.

The need for standard reference materials is illustrated in Table 3.1.

### 3.1.1. SRM 1573 Tomato Leaves

The standard reference material used in the Botany Department laboratory in Bristol was:

Sample : SRM 1573, tomato leaves
Supplier : National Bureau of Standards, Washington D.C. 20234

0.5 grams of tomato leaves were digested for 1 hour in 10mls concentrated Aristar $HNO_3$ and then diluted to 50mls in deionised water before filtering through Whatman No.1 filter paper. All glassware, funnels etc. were cleaned first (overnight) in laboratory detergent (2% Decon 90) and then 10% $HNO_3$, before being rinsed at least twice in deionised water. Results are given in Table 3.2.

The results for flame AAS analyses indicate that standards for the burning conditions used were adequate. The accuracy for lead and zinc may be further improved if the sample number, n = 3, was increased to n = 5 or 10. Samples analysed by ET-AAS indicate that cadmium data were respectable, but that lead values were inadequate for off-the-wall analysis.

**Table 3.2 Concentrations of Cd, Cu, Pb and Zn in NBS SRM 1573 Tomato Leaves Calculated From Their Working Concentration Curves**

| Element | FAAS[1] | Off-The-Wall GFAAS[2] | Certified Value | |
|---|---|---|---|---|
| Cd | 2.96 (±0.14) | 2.87 (±0.15) | 3* | |
| Cu | 11.59 (±0.21) | - | 11 | (±1) |
| Pb | 6.63 (±0.58) | 2.29 (±0.20) | 6.3 | (±0.32) |
| Zn | 66.50 (±2.35) | - | 62 | (±6) |

1 = Flame AAS 2 = Graphite Furnace AAS * = Non-Certified Value

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## 3.1.2. Quasi-Independent Techniques for Determining Accuracy on GFAAS

As well as standard reference materials, other procedures can be used to determine the accuracy of GFAAS. The most commonly employed technique is standard additions. In principle, this is a very useful technique which effectively minimises the differences between standard and sample solutions in their chemical and physical properties. This is achieved by preparing all standards from the sample solution (see Table 3.3 and Fig.3.1). If the standard addition calibration plot gradient is equivalent to the normal calibration plot gradient then negligible chemical interference can be assumed. In this instance the standard additions technique is unnecessary. If the slopes of the calibration plots do not run parallel then interferences must be assumed. The problems that face the use of standard additions have been highlighted in

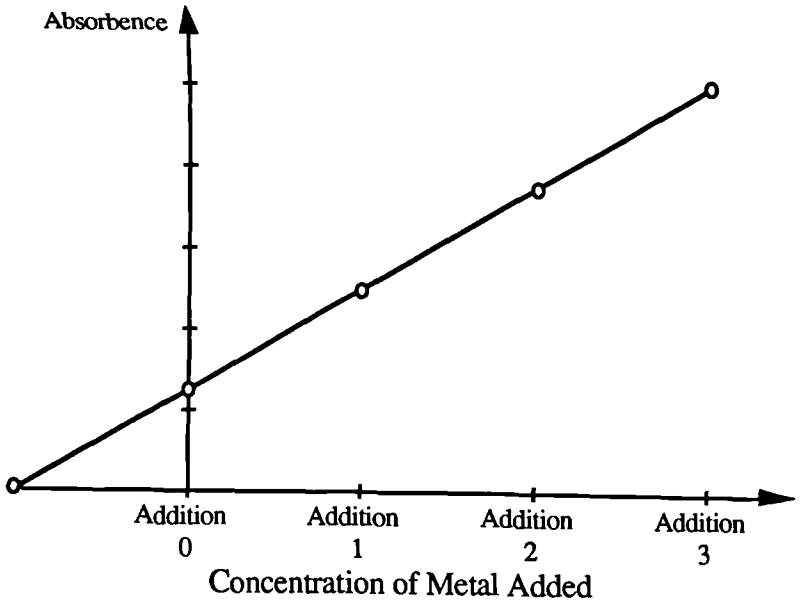


Figure 3.1 Standard addition curve (calibration graph)

## Table 3.3 Example of Standard Additions Dilution Scheme

| | Solution Number | Sample Volume | Added Analyte Volume | Any Added Reagents | De-ionised Water | Analyte Conc. in Final Solution |
|---|---|---|---|---|---|---|
| Blank | 1 | - | - | $1cm^3$ | $9cm^3$ | |
| Zero Addition | 2 | $5cm^3$ | - | $1cm^3$ | $4cm^3$ | ≈0.02ppm |
| Addition 1 | 3 | $5cm^3$ | $1cm^3$ of 0.2ppm std | $1cm^3$ | $3cm^3$ | ≈0.04ppm |
| Addition 2 | 4 | $5cm^3$ | $2cm^3$ of 0.2ppm std | $1cm^3$ | $2cm^3$ | ≈0.06ppm |
| Addition 3 | 5 | $5cm^3$ | $3cm^3$ of 0.2ppm std | $1cm^3$ | $1cm^3$ | ≈0.08ppm |

Section 2.4. The main problem that faces the use of this technique for the samples collected in this thesis is the lack of sample volume to work with to make up the addition standards, especially as regards the metal speciation program (see Chapter 4 Section 4). For this reason, the technique becomes impossible unless the manual technique is used; the manual technique is, however, extremely time consuming. It is also difficult to inject manually the micro-litre volumes, which are applicable to these devices, reproducibly into the atomiser (Van Loon 1985).

The use of standard additions is very useful for low volatile elements such as cadmium, zinc and lead, where interferences can be more marked. Copper is a much easier metal to deal with and high ashing temperatures can be employed for this element, even with off the wall atomisation. All zinc analyses in this thesis were carried out on flame AAS and therefore problems for this element do not arise. Cadmium and lead are the two elements of concern. One way to allay fears about results from GFAAS for cadmium and lead was to compare data collected where both flame and furnace techniques have been employed. Table 3.4 shows some data for the water extract heavy metal speciation technique (see Chapter 4 Section 4), and Table 3.5 data from the *Holcus lanatus* bioassay (see Chapter 5 Section 3). The data from GFAAS appear to relate fairly well to the data for FAAS for both cadmium and copper. The data for lead is not as easy to interpret because of the bad detection limit that lead has on flame AAS. Nevertheless, from the two tables there is some assurance that off-the-wall GFAAS analysis for cadmium and copper is sufficient to produce acceptable results in the speciation procedure and the bioassay.

The speciation procedure (Chapter 4 Section 4) initially used SEP-PAK $C_{18}$ cartridges to separate high polar and low polar metal species. This effectively separated higher molecular weight organics (low polar species) from the rest of the solution and perhaps aided the GFAAS analyses of all the different metal species fractions. Pre-filtering the soil solution through a 0.45μm filter also probably helped analyses. The *Holcus lanatus* samples ought perhaps to have been more prone to interference effects due to the digestion of organic plant material; but again matrix interference appeared to be negligible for copper and cadmium, and seemed not to have been considerable for lead. The very low plant material dry weights used in the acid digests should mean that interfering factors ought not to be as conspicuous as they could otherwise be.

Other research has found the comparison of flame AAS and GFAAS results useful, where in many instances matrix interference has been shown to be

**Table 3.4** **Comparison of Flame AAS and Furnace AAS Methods for Cadmium, Copper and Lead in Different Samples from the Metal Speciation Procedure in Chapter 4, Section 4**

Cadmium mg/l

| Fraction | Fermentation Layer FAAS | | Fermentation Layer GFAAS | | 0-1cm Layer FAAS | | 0-1cm Layer GFAAS | | 8.5-11cm Layer FAAS | | 8.5-11cm Layer GFAAS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| High Polar | 0.013 | (±0.002) | 0.013 | (±0.001) | 0.007 | (±0.001) | 0.006 | (±0.000) | 0.009 | (±0.001) | 0.008 | (±0.000) |
| Low Polar | 0.001 | (±0.001) | 0.002 | (±0.000) | 0.000 | (±0.001) | 0.001 | (±0.000) | 0.001 | (±0.001) | 0.001 | (±0.000) |
| Anionic + Neutral | 0.001 | (±0.001) | 0.002 | (±0.000) | 0.000 | (±0.000) | 0.001 | (±0.001) | 0.000 | (±0.001) | 0.001 | (±0.000) |
| Cationic + Neutral | 0.012 | (±0.002) | 0.012 | (±0.002) | 0.006 | (±0.001) | 0.007 | (±0.000) | 0.008 | (±0.001) | 0.008 | (±0.001) |
| Neutral | 0.000 | (±0.001) | 0.001 | (±0.000) | 0.000 | (±0.000) | 0.001 | (±0.000) | 0.000 | (±0.001) | 0.001 | (±0.000) |

Copper mg/l

| Fraction | Fermentation Layer FAAS | | Fermentation Layer GFAAS | | 0-1cm Layer FAAS | | 0-1cm Layer GFAAS | | 8.5-11cm Layer FAAS | | 8.5-11cm Layer GFAAS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| High Polar | 0.055 | (±0.001) | Over-Range | | 0.034 | (±0.007) | 0.038 | (±0.005)* | 0.029 | (±0.001) | 0.026 | (±0.003) |
| Low Polar | 0.029 | (±0.003) | 0.029 | (±0.002) | 0.011 | (±0.004) | 0.016 | (±0.001) | 0.009 | (±0.004) | 0.009 | (±0.004) |
| Anionic + Neutral | 0.039 | (±0.002) | 0.040 | (±0.001)* | 0.022 | (±0.002) | 0.021 | (±0.003) | 0.017 | (±0.003) | 0.015 | (±0.002) |
| Cationic + Neutral | 0.018 | (±0.003) | 0.019 | (±0.004) | 0.013 | (±0.002) | 0.012 | (±0.003) | 0.013 | (±0.003) | 0.011 | (±0.003) |
| Neutral | 0.004 | (±0.003) | 0.003 | (±0.001) | 0.005 | (±0.002) | 0.004 | (±0.001) | 0.004 | (±0.001) | 0.003 | (±0.001) |

Lead mg/l

| Fraction | Fermentation Layer FAAS | | Fermentation Layer GFAAS | | 0-1cm Layer FAAS | | 0-1cm Layer GFAAS | |
|---|---|---|---|---|---|---|---|---|
| High Polar | 0.30 | (±0.03) | Over-Range | | 0.04 | (±0.01) | 0.029 | (±0.001) |
| Low Polar | 0.06 | (±0.01) | 0.050 | (±0.004) | 0.01 | (±0.01) | 0.013 | (±0.001) |
| Anionic + Neutral | 0.06 | (±0.01) | 0.048 | (±0.008) | 0.01 | (±0.01) | 0.015 | (±0.000) |
| Cationic + Neutral | 0.19 | (±0.03) | Over-Range | | 0.03 | (±0.01) | 0.030 | (±0.002) |
| Neutral | 0.01 | (±0.01) | 0.008 | (±0.001) | 0.00 | (±0.01) | 0.007 | (±0.001) |

* : Sample over-range for GFAAS standards

**Table 3.5 Comparison of Flame AAS and Furnace AAS Methods for Cadmium, Copper and Lead in Different Samples from the *Holcus lanatus* Bioassay in Chapter 5 Section 3**

Metal Concentration mg/l

| Layer Hallen Soil | Cadmium | | Lead | | Copper | |
|---|---|---|---|---|---|---|
| | FAAS | GFAAS | FAAS | GFAAS | FAAS | GFAAS |
| 0-1cm A | 0.016 | 0.014 | 0.03 | 0.022 | 0.044 | 0.040* |
| B | 0.009 | 0.010 | 0.05 | 0.037 | 0.070 | 0.063* |
| C | 0.014 | 0.014 | 0.04 | 0.028 | 0.036 | 0.034* |
| D | 0.007 | 0.006 | 0.02 | 0.021 | 0.063 | 0.057* |
| E | 0.016 | 0.017 | 0.03 | 0.025 | 0.038 | 0.034* |
| F | 0.011 | 0.009 | 0.04 | 0.030 | 0.051 | 0.048* |
| G | 0.008 | 0.008 | 0.04 | 0.030 | 0.027 | 0.026 |
| H | 0.024 | 0.025 | 0.05 | 0.043 | 0.060 | 0.052* |
| I | 0.007 | 0.006 | 0.03 | 0.028 | 0.035 | 0.032 |
| J | 0.008 | 0.006 | 0.04 | 0.029 | 0.029 | 0.026 |
| $\bar{x}$ | 0.012 | 0.012 | 0.04 | 0.029 | 0.045 | 0.041 |
| s.d. | 0.005 | 0.006 | 0.01 | 0.007 | 0.015 | 0.013 |
| 1-3.5cm A | 0.009 | 0.008 | 0.01 | 0.009 | 0.026 | 0.026 |
| B | 0.020 | 0.020 | 0.01 | 0.009 | 0.038 | 0.035 |
| C | 0.009 | 0.008 | 0.02 | 0.011 | 0.031 | 0.029 |
| D | 0.007 | 0.005 | 0.01 | 0.005 | 0.025 | 0.021 |
| E | 0.010 | 0.011 | 0.01 | 0.009 | 0.041 | 0.038 |
| F | 0.005 | 0.006 | 0.01 | 0.009 | 0.024 | 0.023 |
| G | 0.008 | 0.067 | 0.01 | 0.007 | 0.022 | 0.021 |
| H | 0.006 | 0.006 | 0.03 | 0.015 | 0.044 | 0.039 |
| I | 0.007 | 0.007 | 0.02 | 0.011 | 0.033 | 0.030 |
| J | 0.007 | 0.005 | 0.01 | 0.008 | 0.022 | 0.022 |
| $\bar{x}$ | 0.009 | 0.008 | 0.01 | 0.009 | 0.031 | 0.028 |
| s.d. | 0.004 | 0.004 | 0.01 | 0.003 | 0.008 | 0.007 |

* : Samples over-range for GFAAS standards

**Table 3.6 Concentration of Lead in NBS Standard Reference Materials Calculated from the Working Curve and by Standard Addition**

| | | Tube Wall | | Platform | |
|---|---|---|---|---|---|
| NBS Reference Material | Certified Value (μg/g) | Working Curve | Std. Addn. | Working Curve | Std. Addn. |
| Bovine Liver#1557 | 0.34 ±0.08 | <0.1 | <0.1 | 0.46 | 0.55 |
| Oyster#1566 | 0.48 ±0.04 | <0.2 | <0.2 | 0.42 | 0.58 |
| Tuna#50 | (0.46)[a] | 0.23 | 0.47 | 0.62 | 0.60 |
| Spinach#1570 | 1.2 ±0.2 | 0.45 | 1.0 | 0.85 | 1.5 |
| Tomato Leaves#1573 | 6.3 ±0.3 | 1.9 | 4.5 | 3.2 | 5.5 |
| Pine Needles#1575 | 10.8 ±0.5 | 6.2 | 10.5 | 8.5 | 12.6 |

minimal e.g. cadmium in plant material and soil extracts (Ure and Mitchell 1976), cadmium and lead in fertilisers and plant tissues (Woodis *et al.*1977), and cadmium, copper and lead in sewage sludge (Carrondo *et al.*1979a, 1979b, Lester *et al.*1977, Stoveland *et al.*1979).

## 3.1.3. Lead and GFAAS Interferences

Flameless atomiser determinations of lead in environmental samples suffer frequently from interferences of various nature (Callio 1980). Interference of lead is often due to one or more of the following effects (Hodges 1977):

(a) The presence of variable amounts of both cations and anions e.g. magnesium and sulphate, which inhibit the atomisation process, resulting in variable lead sensitivity.

(b) Non-specific absorption or light scattering by molecular vapours of the salt matrix.

(c) The loss of lead as a volatile halide during ashing in the presence of high salt concentrations.

The use of a L'vov platform leads to a reduction in vapour-phase interferences and less effect on the analyte signal from matrix-dependent variations in appearance temperature, but does not necessarily rule out all interferences in complex samples (Hinderberger *et al.*1981). The effect of $MgCl_2$ on Pb signal from a platform and off-the-wall atomisation is illustrated in Fig.3.2. Hinderberger *et al.*(1981) illustrated how complex sample solutions from NBS standard reference materials can affect lead determination even when a platform is used (Table 3.6).

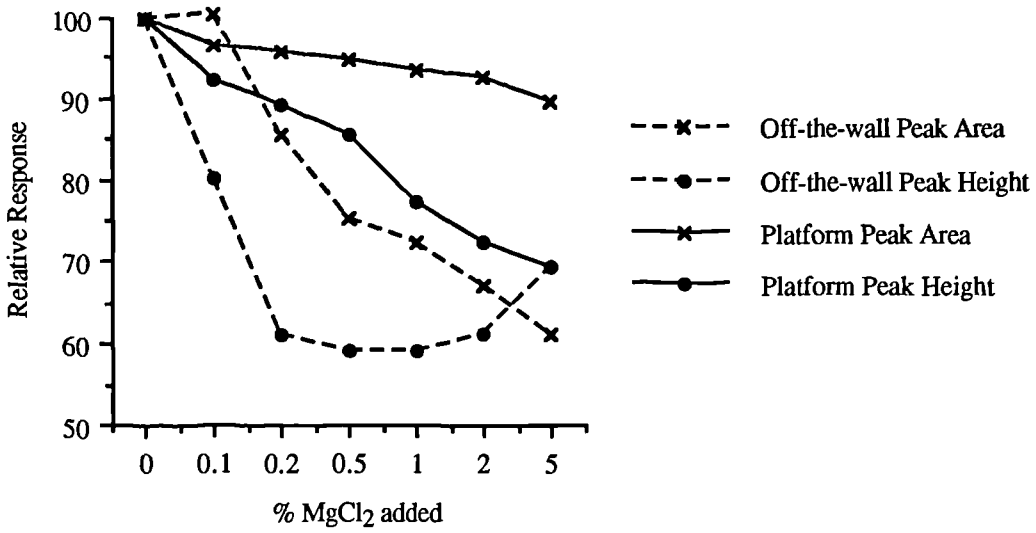


Figure 3.2 Effect of $MgCl_2$ on Pb signal from a platform and off-the wall (Dymott 1985)

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Chemical modifiers are commonly employed to improve the determination of lead e.g. $NH_4H_2PO_4$ (Hinderberger *et al.* 1981), $H_3PO_4$ (Hughes 1977, Callio 1980), $NH_4NO_3$ (Ediger *et al.* 1974), $NH_4H_2PO_4$ + $Mg(NO_3)_2$ (Bettinelli *et al.* 1986), and others (e.g. see Holcombe and Bass 1988). It might be argued that chemical modifiers should have been used for determining lead in the heavy metal speciation procedure (Chapter 4 Section 4) and *Holcus lanatus* (Chapter 5 Section 3) samples. Tramontano *et al.* (1987) found that direct determination of Cd, Cu, Pb and Zn by GFAAS was sufficient for precipitation samples. They stated that the major ion matrix gave no problems for Cd, Cu and Zn determination; but for Pb there was significant signal suppression. The use of a platform eliminated matrix suppression of Pb and the need for standard additions. Other reports indicate that there can be a lack of matrix interference from plant materials and soil extracts (Ure *et al.* 1978, Woodis *et al.* 1977).

## 3.2. Contamination

Certain elements such as Zn, Ca, K, Na and Fe can be fairly ubiquitous in laboratory environments. Three forms of contamination can occur:

(a) +ve addition of analyte contaminant.
(b) -ve losses of analyte.
(c) Pseudo-contamination - due to substance other than the analyte.

Certain aspects of laboratory preparation have to be taken into close consideration to avoid contamination:

(a) Quality of water.
(b) Precipitation of standards and calibration solutions.
(c) Choice of reagents.
(d) Choice of bottles for storage of samples and standard solutions.

### 3.2.1. Water Purity

High purity water is best as trace metal analyses are usually in the µg/l range. It is best to use water with a high resistivity, better than 10MΩ/cm, and total solids < 1µg/ml. Distillation and/or deionisation of water is commonly employed to achieve this. Bristol Botany Department laboratories use a combination of both techniques.

### 3.2.2. Reagent Quality

In most circumstances Analar reagents are of a high enough purity to be used; but for GFAAS Aristar reagents should be utilised. Long term storage can degrade the quality of chemicals. Reagent blanks should always be run in trace element analyses (preferably at least three blanks per sample set).

### 3.2.3. Standard Solution Preparation

Normally 100-1000mls of 1000-10,000µg/ml of the analyte of interest is prepared as a stock solution from which lower concentration standards can be obtained. Creating a stock solution with a high concentration of the analyte ensures accurate weighing of the analyte for standard preparation and also can make the standard solutions stable for up to one year (especially if they contain 1% acid - usually $HNO_3$ or HCl). In this thesis all standards and samples were preserved in 20% $HNO_3$. Usually the metal or a simple salt of the metal is used to make the stock solution (Analar grade is usually sufficient); stock solutions are also now commercially available. The less concentrated the stock solution, the less stable it is. Therefore, for GFAAS work, it is best to make fresh standards fairly regularly. The recommended preparation of element stock solutions is shown in Table 3.7.

**Table 3.7 Preparation of Element Stock Solutions (Pye Unicam Ltd)**

| Element | Reagent | Weight (g) | Dissolution | 1000mg/l of |
|---|---|---|---|---|
| Cd | CdO | 1.1423 | 20ml 5M-HCl | Cd |
| | Metal rod | 1.0000 | 20ml 5M-HCl + 2 drops conc. $HNO_3$ | Cd |
| Cu | Metal foil | 1.0000 | 50ml 5M-$HNO_3$ | Cu |
| Pb | Metal sheet | 1.0000 | 50ml 2M-$HNO_3$ | Pb |
| Zn | Metal chips | 1.0000 | 30ml 5M-HCl | Zn |
| | Metal chips | 0.8040 | 30ml 5M-HCl | ZnO |

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### 3.2.4. Containers

Contamination or sorption loss depends on:

(a) The chemical form/concentration of the analyte element.
(b) Solution parameters: pH, dissolved salts, complexing agents, dissolved gases, suspended material, micro-organisms.
(c) The container: chemical composition of walls, surface roughness, surface cleanliness (e.g. clean in 8M $HNO_3$), surface area exposed to solution.
(d) External factors: length of storage, temperature, light exposure and agitation.

## 4. Sample Preparation (Acid Digestion)

All soil material was disaggregated to pass through a 2mm sieve. All material for analysis of total metal concentration was oven dried at 80°C. All decomposition of sample materials was carried out in borosilicate glassware. All glassware was cleaned in laboratory detergent (2% Decon 90) overnight and then 10% $HNO_3$ overnight. Sample decomposition entailed the used of concentrated $HNO_3$ (usually 1g or less of sample material to 10mls of acid). Concentrated $HNO_3$ alone (e.g. at 100°C for one hour on a thermostatically controlled metal heating block) has a less vigorous effect than a mixed acid digest (e.g. perchloric acid and nitric acid) and, in particular, Fe(III) oxide minerals are not attacked strongly. However, concentrated nitric acid alone is

an efficient method for Cd, Cu, Pb and Zn (Thompson 1983). Use of perchloric acid and nitric acid does produce a more efficient breakdown of organic matter, but has drawbacks:

(a) Higher cost.
(b) Explosive hazard.
(c) Formation of sparingly soluble potassium perchlorate crystals that occlude trace metals.

# 5. Sensitivities and Detection Limits/Precision and Accuracy

## 5.1 Sensitivity and Detection Limit

These are an expression of the analytical performance of an AAS. Sensitivity is defined as that concentration of the element in µg/ml in aqueous solution which gives an absorbence of 0.00436 (≡ 1% absorption of the transmitted radiation). Optimum concentration ranges (for optimum analytical precision) generally lie between 20 and 200 times the sensitivity figure.

Detection limit is defined as the concentration of an element, in µg/ml, which gives a reading = 2x the standard deviation of the background signal (from 10 sequential readings).

## 5.2 Precision and Accuracy

Sources of error in the atomic absorption system are:

(a) Fluctuations in hollow cathode lamp emission signal.
(b) Photomultiplier "shot noise".
(c) Electronic (Johnson) "noise".
(d) Flame fluctuation.
(e) Nebulisation and atomisation "noise".
(f) Inaccuracies in the readout system.
(g) Systematic and random errors incurred in sample preparation.
(h) Inter-element interferences.

Precision (or relative standard deviation) is a measure of the validity of a set of results. Poor precision indicates a wide spread of individual results and therefore less confidence in their accuracy as calibration or sampling points.

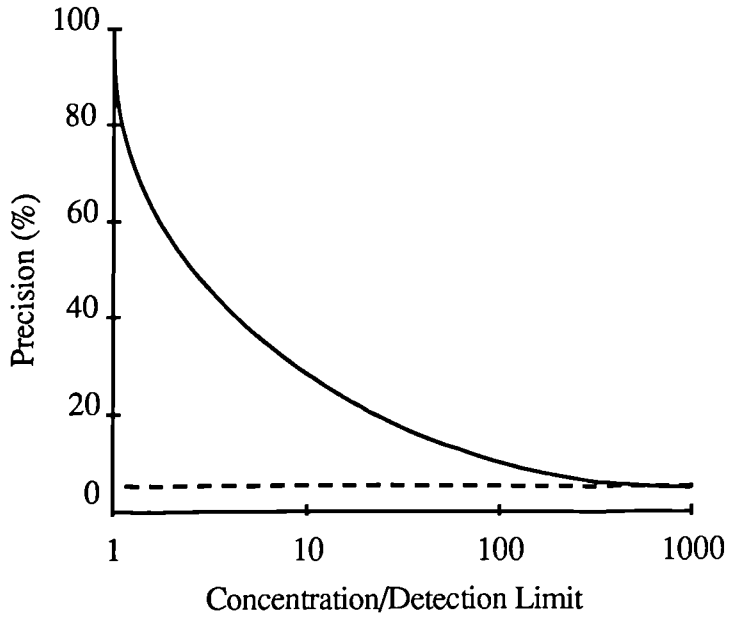


Figure 5.1 Precision expressed as a function of analyte concentration (c) divided by the detection limit (Cd), during the rapid determination of trace elements in geological materials by AAS. The precision (=twice the coefficient of variation expressed as a percentage) falls from 100% at c/Cd = 1 asymptotically towards a constant value of 6% at high concentrations

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The precision improves as the concentration of an analyte in relation to its detection limit increases (see Fig.5.1 after Thompson 1983).

*Accuracy is the closeness of* $\bar{c}$ *(the central tendency of a distribution* - usually the arithmetic mean) to the true value. Accuracy is limited mainly by interference effects (see Fig.5.2 after Thompson 1983).

Accuracy and precision relate to the following equation for standard deviation ($S_c$):

$$S_c = \sqrt{\frac{\Sigma\ (c_i - \bar{c})^2}{(n - 1)}}$$

$c_i$ : recorded value
$\bar{c}$ : mean of observations
n : number of observations

The closeness of $\bar{c}$ to the true value = accuracy.
Relative variation 2 Sc / $\bar{c}$ = precision.

$$\text{Precision} = \text{relative standard deviation} = \frac{(S_c \times 100)}{\bar{c}}\ \%$$

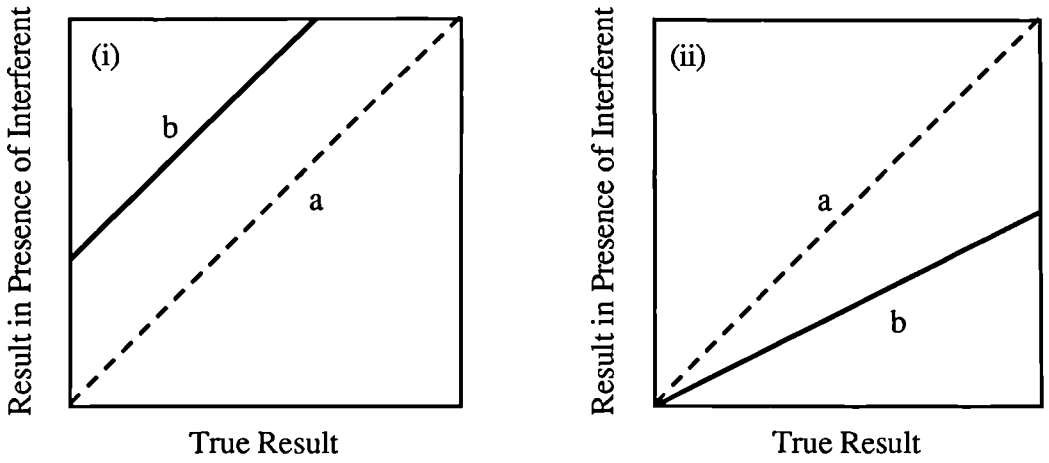


Figure 5.2 Schematic account of possible biases produced by a fixed level of interferent in the determination of trace elements by AAS, VIZ :

(i) "Translational" (constant) bias usually caused by background absorption
(ii) "Rotational" (proportional) bias due inter alia to changes in atomisation efficiency (a = no interferent present, b = interferent present at a fixed level)

# APPENDIX B

# ANION ANALYSIS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

## 1. The Historical Development of Liquid Chromatography

In 1906 Tswett, a Russian botanist, observed that plant pigments could be separated by eluting with petroleum from a calcium carbonate bed - the separation being termed 'chromatography' ("colour writing"). In the early 1940's the theory of liquid chromatography was proposed. For this Martin and co-workers were awarded the Nobel Prize is 1952. Little advance was made except in amino acid analysis, where a photometry detection system was produced. Then, in the late 1960's, a 254mm ultraviolet (U.V.) detector was designed. With a suitable detector available, advances were quickly to ensue: variable wavelength U.V., micro-particulates, fluorescence, refractive index, bonded phases, gel permeation etc. were all incorporated into the technique. It is perhaps only in the past 15 years that liquid chromatography has received prominence in metal and non-metal (inorganic) analysis of species.

## 2. Principles of High Performance Liquid Chromatography

The differential migration process, in which sample components are dissolved in a mobile phase and are selectively retained by a stationary phase, is called chromatography. The separation of component species in the mobile phase is due to species differences in their distribution coefficients:

$$K = \frac{C_s X}{C_m X}$$

K : distribution coefficient
X : chemical species X
$C_s$ : stationary phase conc.
$C_m$ : mobile phase conc.

Rate of migration (RM) of species X is inversely proportional to K or the capacity factor. Therefore, the higher the distribution of X in Cs the slower it will move through the column. RM and K are affected by the experimental variables:

(a) Temperature.
(b) Composition of the stationary phase/column substrate.
(c) Composition of the mobile phase/eluent.

The capacity factor, K', is a function of the retention time of the species X and the solvent front:

$$K' = \frac{t_r - t_o}{t_o}$$

$t_r$ : component retention time
$t_o$ : solvent front retention time

The selectivity $\propto$ is used when the distribution of two different components are related to one another:

$$\propto = \frac{K_1'}{K_2'}$$

The values will remain constant for a given set of conditions. The separation between two peaks is called Resolution (Rs):

$$Rs = \frac{1}{4} \cdot \frac{\Delta K'}{K'} \cdot \frac{K'}{1 + K'} \cdot \sqrt{N}$$

Selectivity | Degree of Retention | Column Efficiency

N = Plate number K' = Capacity factor

The plate number is a function of the retention time and peak width. Changes in the selectivity have the greatest effect on Rs.

The basic chromatographic scheme is illustrated in Fig.2.1.

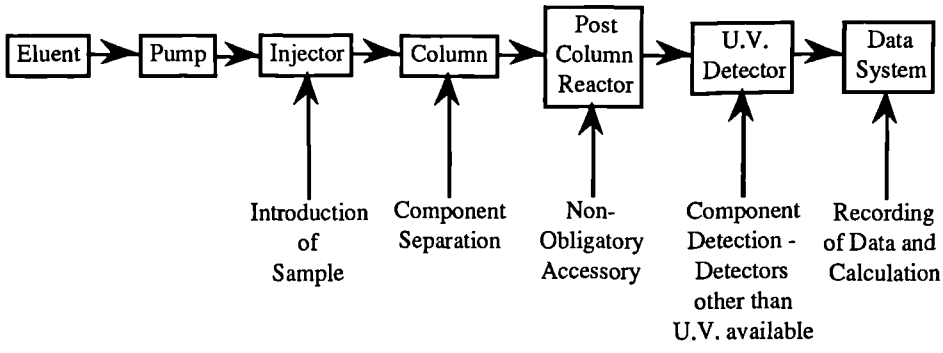


Fig.2.1 Liquid chromatography schematic

As each species component is eluted through the detector a change in electrical output is produced and recorded by and integrator or computer (see Fig.2.2).

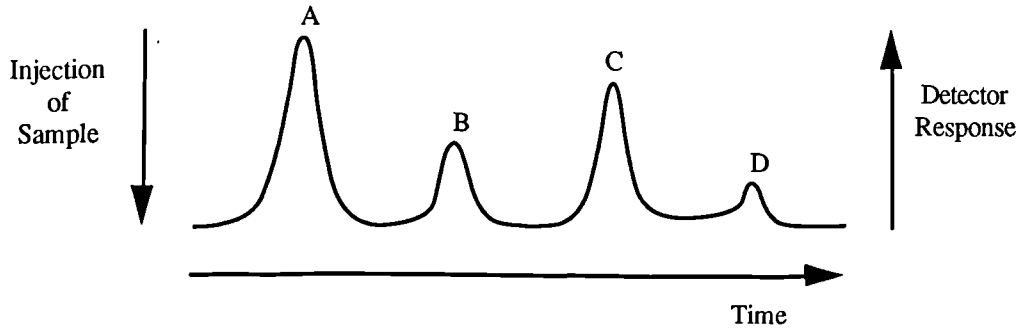


Fig.2.2 Chromatogram output - separation of four individual components

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# 3. Instrumentation

## 3.1 The Pump - Philips PU4015

The most widely used in HPLC are reciprocating piston pumps.

## 3.2 Injection System - Rheodyne 7125 Syringe Loading Sample Injector

The sample is introduced by syringe to a loop which is isolated from the solvent flowing to the column. The mobile phase is redirected through the loop to deliver the sample to the column by switching the valve connection. The loop volume governs the sample size.

## 3.3 The Ultraviolet Detector - Philips PU4025

In principle, the electrical response of a detector should be linearly proportional to the concentration of the component in the sample being analysed, assuming that a stable baseline is present. The resulting chromatogram could be easily used for quantitative analysis. In practice, however, the linear response will only work over a restricted working range in most instances (see Fig.3.1).

U.V. absorption detectors are the most widely used detector. Absorbance of U.V. radiation by a compound is due to a change in internal energy of the

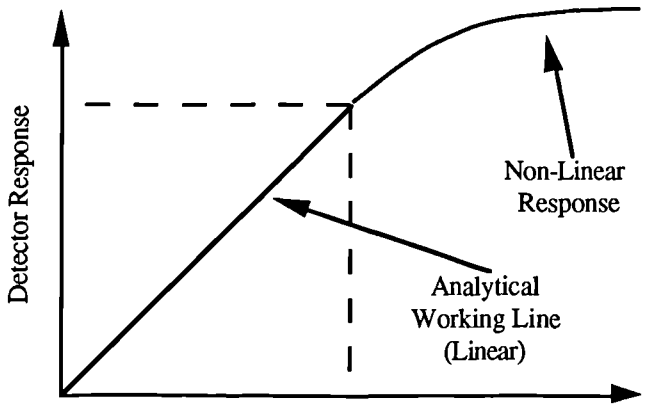


Figure 3.1

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molecules caused by a change in electron configuration. Compounds containing only saturated bonds exhibit very little U.V. absorption compared with unsaturated compounds. The greater the number of unsaturated bonds the more the absorbance increases. The chromophore is the part of the molecule that provides the main U.V. absorption. A particular section of a molecule can affect the absorbance spectrum of that molecule (e.g. the wavelength of maximum absorbance) or can intensify or reduce the absorbance. Generally, polar groups such as $-NH_2$ or $-NO_2$ can alter the absorption spectrum of the parent molecule, whereas non-polar groups such as $-CH_3$ have much less of an effect.

The absorption of U.V. radiation is governed by the Beer Lambert law - the same principle as explained for atomic absorption spectrophotometry (see Appendix A). The U.V. radiation is supplied by a deuterium lamp which can operate over a wavelength range of 190-380nm. The incident beam passes through a flow cell and its intensity is measured by a photocell.

The data system used to record signal response was a Spectra-Physics SP4270/SP4290 Integrator.

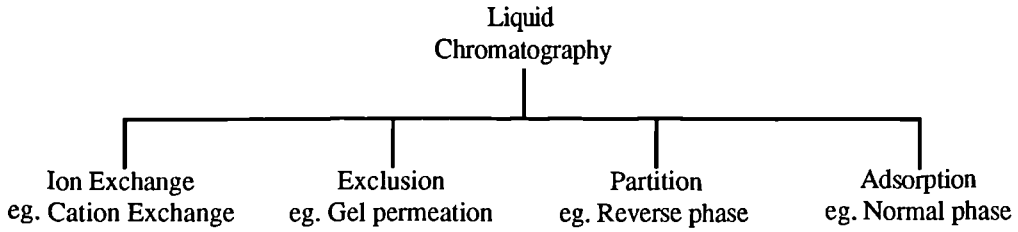


Fig. 4.1

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# 4. Theory and Application of Anion Exchange Chromatography

## 4.1. Introduction

The separation modes involved in liquid chromatography are shown in Fig.4.1.

The relative usage of the 4 main separation modes indicates that ion exchange techniques only obtain 5% relative usage. This is probably as a result of reversed phase ion pairing techniques also being used for ionic and ionisable compound separation. Fig.4.2 denotes a column selection chart indicating which columns may be used for which purpose. The column that was used in this thesis for inorganic anion separation was a VYDAC 302IC column, employed for ion exchange chromatography.

## 4.2. Method of Ion Exchange Chromatography

The separation, identification and quantitation of ionic species is of particular importance in a number of fields of research: agricultural, medicinal, industrial, the food industry, the photographic industry, plating industry and petroleum refining industry etc. To cope with complex mixtures of ions, from which ion-selective electrodes can suffer interference, the technique of ion-exchange chromatography has been developed: becoming routinely employed since 1975 (Small *et al.*1975).

The functional group, upon the stationary phase of the column (usually a modified silica or resin), contains a fixed ionic size. Quaternary ammonium groups, $-R_3N^+$, are often employed for anionic exchange. An exchangeable counter ion is always associated with the functional group to give electrical neutrality. The quaternary ammonium group is strongly basic in the OH form

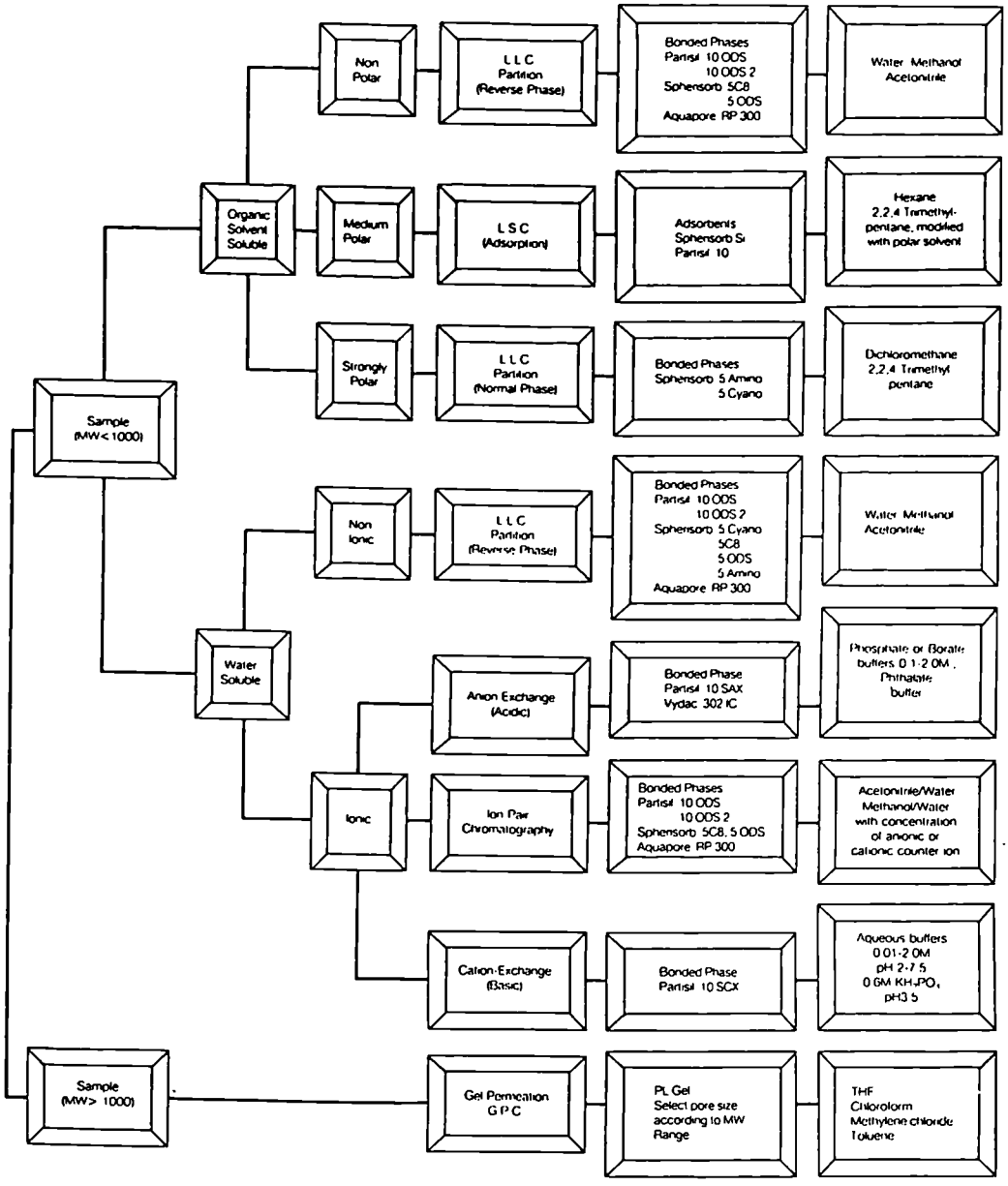


Fig.4.2. Column selection chart

and can dissociate totally so that its exchange properties are thus independent of the pH of the mobile phase. Anions in the sample can be exchanged with the counter ion, so becoming associated with the fixed functional group ionic site (anionic retention by the column). Different anions will have differing affinities for the functional ionic site, allowing separation of different anion species. The retention time of each anionic species is affected by a number of parameters including:

(a) The size and charge of the sample ion.
(b) The pH of the mobile phase.
(c) The total concentration and type of counter ions in the mobile phase.
(d) The presence of organic solvents (such as methanol) in the mobile phase.
(e) Column temperature.

Processes such as adsorption and partition may also play a role in ion separation which can make it more difficult to predict the behaviour of ion exchange columns for particular analyses. The stationary phase materials for anion separation fall into three basic classes (see Table 4.1).

The pellicular silica was developed by the Separations Group (Hesperia, California) and marketed under the trade name VYDAC 302. It has a surface area of $86m^2/g$ (≡ a microporous gel resin). The pH range of this material, $Si-(CH_2)_n-NR_3^+C_1^-$ (for anion exchange), is limited (pH 2-7) because of the silica backbone and the lability of the silyl bond. Therefore these are limitations on the choice of eluting ion and the working pH. Its anion selectivity is also somewhat different to that of conventional organic-based materials. Lower relation of anions is achieved because of the low exchange capacity packing, which therefore enables the use of weaker counter ion concentrations (e.g. phthalate ions) allowing higher sensitivities to be produced (e.g. see Cochrane and Hillman 1982).

## 4.3. Indirect U.V. Detection in Ion Exchange Chromatography

The solvent used, with U.V. detection HPLC work, usually has a low absorbence at the working wavelength. This means that, when the species under study passes through the detector, absorption of energy can occur. Absorbance due to chromophores causes a decrease in transmission of energy through the flowcell resulting in a positive peak response on the chart recorder;

**Table 4.1 Materials Commonly Used in IC or Anion Chromatography (after Pohl and Johnson 1980)**

| Material | Particle Shape | Capacity (meq/l) | Range | pH Range | Availability |
|---|---|---|---|---|---|
| Pellicular Silica | Spherical | Low capacity | 20μ | 2-7 | Separations group VYDAC 302 |
| Surface Aminated Macroporous Resin | Irregular | 0.007-0.07 | 44-57μ | 0-14 | Not commercially available |
| Latex agglomerated | Spherical | 0.02-0.05 | 20-30μ | 0-14 | Dionex Corp. anion separators |

but if the mobile phase solvent is a weak absorber of U.V. light at the working wavelength and non-U.V. absorbing species are present in the element, then transmission of energy through the flowcell increases and a negative peak response results. This latter response is indirect U.V. detection (see Fig.4.3) and can be used for inorganic ions which are mainly considered to be non-U.V. absorbers. It is common practice to reverse the polarity of the input to the recorder so that the ionic species of interest produce a positive peak response.

Detection by the indirect U.V. method may be 5-1000 times more sensitive that detection by monitoring the conductivity of the eluent (e.g. Cochrane and Hillman 1982, Small and Miller 1982). Conductivity detection may also require the use of suppressor columns (e.g. Girard and Glatz 1981, Pohl and Johnson 1980) which are not required in indirect U.V. detection. The approaches for the determination of inorganic species are shown in Table 4.2 (from Krull 1986). The VYDAC 302IC column falls into the SCIC grouping. The paired-ion reversed-phase method is also proving to be a very popular technique in ion-exchange chromatography (Cooke *et al.*1985, Krull 1986).

## 4.4. The Solvent Eluent (Mobile Phase)

The separation of components in the sample solution depends not only on the stationary phase materials, but also on the mobile phase solvent. The solvent should have the correct chromatographic qualities required for a sample separation and also should be compatible with the detection system in use. A mobile phase solvent should have the following qualities:

(a) Lack of dissolved gases - degassing the solvent prevents the opportunity of gases, such as oxygen and nitrogen, outgassing in pump heads which could cause excessive baseline noise and disharmony in the pumping system. Degassing is achieved by reflux, vacuum pumps, ultrasonic baths or helium purge. A vacuum pump was found to be sufficient for degassing purposes in this thesis, although the fact that gases reabsorbed during elongated analysis periods had to be taken into account.

(b) Solvent polarity - as ions of a polar nature were to be separated, the solvent eluent should also have polarity i.e. compounds that contain fractional groups that exhibit localised electron concentrations so that they

**Table 4.2 Summary of Column Liquid Chromatography Approaches for the Determination of Inorganic Species**

| Name of Method | Operating Principles | Advantages and Disadvantages |
|---|---|---|
| Dual-column, suppressed ion-chromatography (DCIC) | Analytical column (first) performs the desired ionic separations, second stripper (suppressor) column removes back-ground ions from eluent before final detection | Requires and all-glass/plastic system, low-pressure pumping system, special packing materials for separation and suppression, available from but one supplier at high prices, not always compatible with other commercial HPLC equipment, suppression step introduces extra column variances (dead volume) |
| Single-column, non-suppressed ion chromatography (SCIC) | One analytical separation column, low-capacity packing material, low-conductivity eluent mobile phase, conductivity detection | Can be used with almost all commercial HPLC equipment, available at reasonable prices from a number of manufacturers, uses modular system for interchange parts, can be used with variety of detectors from many suppliers, latest chromatography has improved greatly over initial peak shapes/asymmetry factors, resolutions etc. |
| Ion-exchange HPLC | Single analytical ion-exchange column, uses silica or polymeric ion-exchange packings, separations by ion-ion interactions, used with most commercial detectors | Compatible with all commercial HPLC equipment, inexpensive instrumentation/columns, aqueous or aqueous/organic mobile phases, can be used with almost all detectors, chromatographic performance with latest, small-particle packings is excellent, reasonably priced from numerous suppliers |
| Paired-ion reversed-phase HPLC (PIRP) | Single analytical reversed or bonded-phase column, silica or polymeric packings, separates both ionic and neutral species at the same time, compatible with all commercial detectors, separations based on hydrophilic-hydrophobic interactions between aqueous-based mobile phase and hydrocarbonaceous stationary phase, equilibrium distribution of organic/inorganic, ionic/neutral species | Compatible with all commercial HPLC equipment, inexpensive instrumentation/columns, aqueous or aqueous/organic mobile phases, can be used with just about all detectors, chromatographic performance and peak shapes generally excellent, large variety of commercially available bonded phases (bulk or packed) for varying separations, can do both neutral and charged separations in one run for organics and inorganics, compatible with post-column reactions for derivatisation (on-line) |

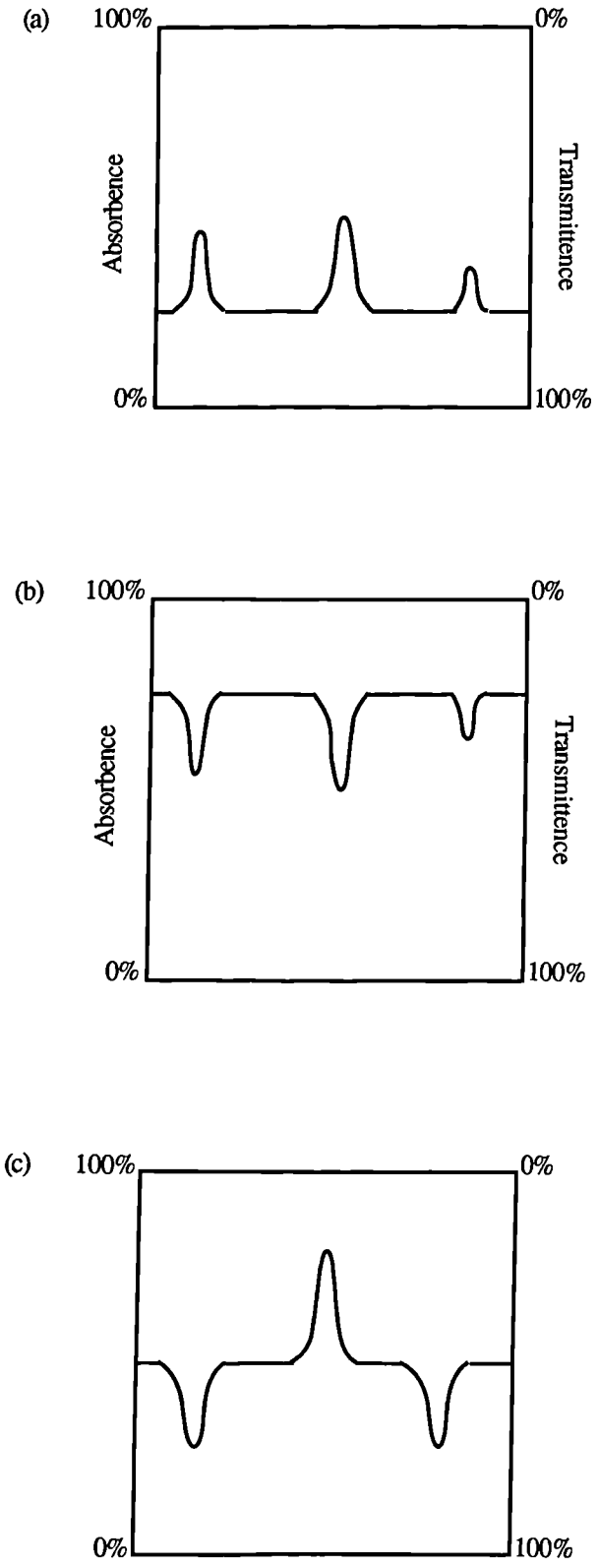


Fig.4.3. The principle of direct and indirect U.V. detection: (a) Positive peak response due to sample absorbance being greater than the eluent absorbance e.g. Cortes (1982), Iskandarani and Pietzyk (1982); (b) Negative peak response due to eluent absorbance being greater than sample absorbance e.g. Cochrane and Hillman (1982), Imanari *et al.* (1982), Dreux *et al.*(1982); (c) Positive and negative peak response e.g. Wheals (1983).

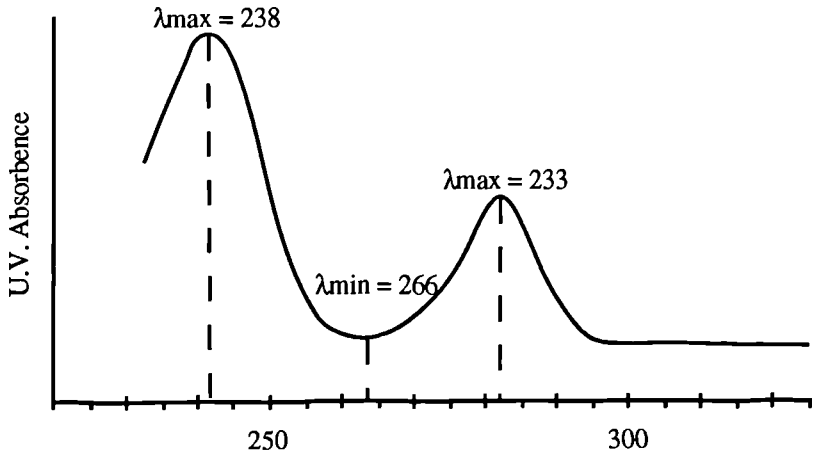


Fig.4.4 The ultra-violet spectrum of potassium hydrogen phthalate at pH=6.3

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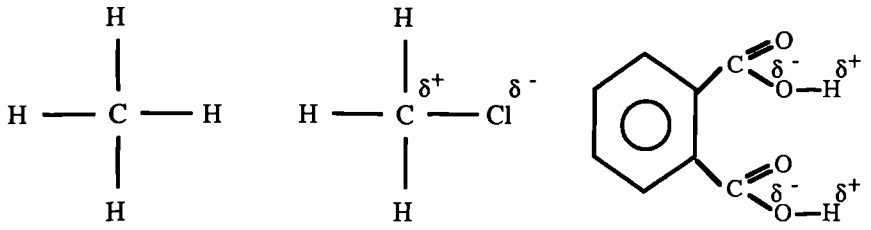
are characterised by a dipole moment. The functional groups that help exert polarity in a substance are -CN, $-NH_2$, -COOH, -OH, Halide etc.



NON-POLAR | POLAR (Diplole Moment) | Phthalic Acid POLAR

(c) U.V. Transparency - essential for HPLC where the detection system is U.V. Thus, in the case of phthalate ions, there are certain windows in the U.V. spectrum that allow the solvent to be used (see Fig.4.4).

(d) Certain physical characteristics - a low molecular weight to reduce the complexity of mass spectra; a boiling point that is not less that 40°C to prevent boiling before being drawn into the pump heads; miscibility where mixtures of solvents are required.

The solvent used as the mobile phase in this thesis was phthalic acid. The recommended eluent for the VYDAC 302 column was 0.002M phthalic acid. The phthalate ion has proved to be very popular as an eluent component: sodium phthalate (Small and Miller 1982), potassium phthalate

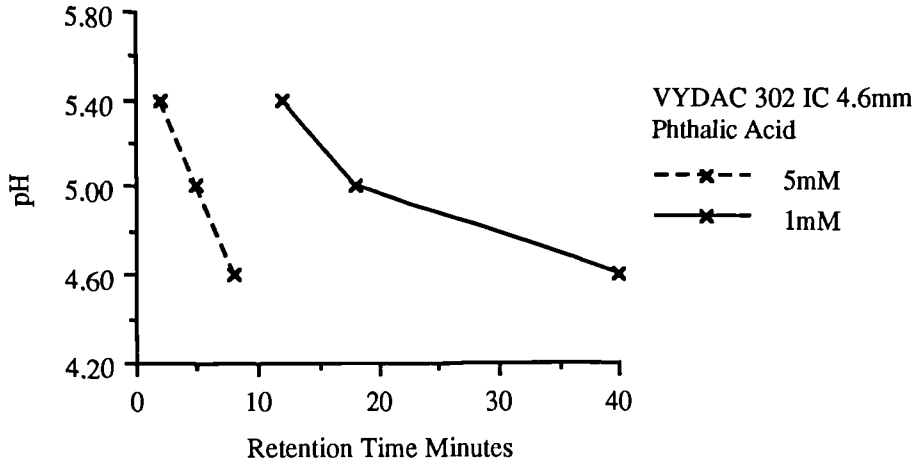



Fig.4.5 The retention time of $SO_4^{2-}$ as a function of Phthalate concentration and pH (redrawn Girard and Glatz 1981)

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(Cooke *et al.*1985, Gjerde *et al.*1979, 1980, Cochrane and Hillman 1982), and phthalic acid (Girard and Glatz 1981, Pohl and Johnson 1980) have all been used. Where U.V. detection was employed, then wavelengths of 266nm (Cooke *et al.*1985) and 308nm (Cochrane and Hillman 1982) were used (see Fig.4.2).

Potassium hydrogen phthalate is a commonly employed solvent. Phthalic acid is also widely used but generally at a lower pH range. The phthalate counterion is an ionic U.V. absorbing compound and so its concentration should be kept as low as possible to give the best sensitivity; but low concentrations also give long analysis times. This means that a practical concentration should be used (generally $5x10^{-3}M$ to $5x10^{-4}M$) to provide a compromise between sensitivity and length of analysis time. Ions such as sulphate that are strongly retained can have their retention times reduced by increasing the phthalate concentration and/or increasing the eluent pH (e.g. with sodium borate). See Fig.4.5.

The effect of eluent pH is also dramatically illustrated by Gjerde *et al.*(1979, 1980). They demonstrate that anions are eluted more rapidly when the eluent pH is raised from 4.4 to 6.75. For sulphate, the effect is very dramatic, probably as a result of more of the phthalate being present as the divalent anion at pH6.1 (see Table 4.3).

**Table 4.3 Adjusted Relation Times (min) of Anions With Phthalate Eluent**

| | XAD-1 (0.04 mequiv/g) | | VYDAC SC (0.1 mequiv/g) | |
|---|---|---|---|---|
| Ion | Phthalate $5x10^{-4}M$ pH = 4.4 | Phthalate $5x10^{-4}M$ pH = 6.1 | Phthalate $5x10^{-4}M$ pH = 4.50 | Phthalate $5x10^{-4}M$ pH = 6.75 |
| $F^-$ | 0.8 | 0.0 | ? | ? |
| $Cl^-$ | 1.3 | 0.7 | 1.70 | 1.12 |
| $NO_2^-$ | 1.4 | 0.8 | 3.24 | 2.12 |
| $Br^-$ | 2.1 | 1.3 | 7.12 | 4.88 |
| $NO_3^-$ | 2.2 | 1.4 | 9.42 | 7.74 |
| $SO_4^{2-}$ | 16.4 | 4.4 | 24.4 | 4.48 |
| $H_2PO_4^-$ | N.A. | N.A. | 1.72 | 1.00 (neg) |

N.A.=not available

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# 5. Qualitative and Quantitative Analysis by HPLC

## 5.1. Qualitative Analysis

This depends on the fact that the retention time or retention volume of any component in the sample remains constant under fixed chromatographic conditions. These conditions are: column dimensions, column packing material, column temperature, mobile phase and flow rate. There are three steps one can take towards the identification of a component peak:

(a) Directly compare the retention times of a pure reference material with that of an unknown sample material run under identical conditions. Also spiking the sample with the pure reference material is another form of comparison.

(b) Repeat the analyses of the unknown sample and reference materials using another column packed with a different type of stationary phase; this means that if two compounds have the same retention time in (a), they should be separated in (b) because two compounds rarely have the same retention time on different stationary phases.

(c) Employ other techniques such as infrared and mass spectrometry in conjunction with liquid chromatography.

Methods (a) and (b) are the most commonly utilised techniques. As mentioned in Section 4.3, paired-ion reversed-phase ion-exchange chromatography is also a useful method for inorganic ion separation. Using this method for anion chromatography, a typical mobile phase would contain a quaternary ammonium salt (to modify the stationary phase), whilst also containing the U.V. absorbing eluting counterion e.g. phthalate, citrate etc. Initially, in this thesis, a method was used that followed a set of conditions reported by Wheals (1983) and used for herbage and soil analysis (Jane 1983). The conditions used were:

| | |
|---|---|
| Column | : 25cm x 4.6mm(I.D.) Spherisorb 5 ODS reverse phase-octadecylsilane. |
| Eluent | : 1.75g citric acid and 0.125g cetyltrimethyl-ammonium-bromide (cetrimide) were dissolved in 2.5 litres of water/methanol (70/30 V/V). The pH was adjusted to 5.5 by addition of 0.880 ammonium hydroxide (approx 20 drops). |
| Flow rate | : 2mls/min* |
| Injection | : 20µl |
| Detection | : U.V. at 220nm |

The performance of this method was less successful than that of the VYDAC 302IC/phthalic acid separation; this may have been due to an older Spherisorb column being used. However, Reeve (1979) also found that investigations using a more conventional ODS column (Spherisorb SIO ODS) with cetrimide were less successful due to poor column efficiency. Possibly use of a phthalate counterion and tetra-n-butyl ammonium hydroxide at 266nm (after Cooke *et al.*1985) may have proved more successful. Nevertheless it was decided to use the VYDAC 302 IC column instead of the Spherisorb 5ODS column.

## 5.2. Quantitative Analysis

The response that a compound produces on the U.V. detector will depend on the compound extinction coefficient. Results calculated on peak height measurements are usually not as reliable as those based on peak area measurements. It is therefore best to use peak area measurements where quantitation can be achieved by the construction calibration curves. The

calibration curves for chloride, nitrate, sulphate and phosphate were produced under the following conditions:

| | |
|---|---|
| Column | : 25cm x 4.6mm(I.D.) VYDAC 302 IC. |
| Eluent | : $1x10^{-3}$M phthalic acid adjusted to pH4.9 with sodium borate. |
| Flow rate | : 3mls/min |
| Injection | : 20µl |
| Detection | : U.V. at 254nm |

Table 5.1 also shows data collected at two different times.Both peak area and peak height measurements seemed adequate for all four anions, and in the case of phosphate the latter measurement was the better option to use. The sensitivities of the anions followed the order:

Chloride > Nitrate > Sulphate > Phosphate

The detection limits were in the order of 0.5ppm for chloride, 0.3ppm for nitrate, 3ppm for sulphate and 3ppm for phosphate. This proved adequate for the analysis of soil solutions for chloride, nitrate and sulphate, but could have been better for phosphate analysis. Sensitivity would have been improved if the phthalate concentration was decreased to $5x10^{-4}$M, but this would have greatly increased the analysis time. By making the monitoring wavelength closer to the $\lambda_{max}$ of the phthalate, higher sensitivity is also attained, but larger back-off on the detector results in poor signal-to-noise ratio. Perhaps the best way to have improved the detection limit of phosphate (and the other anions) would have been to use a larger injection loop (a 50µl loop may have been sufficient).

All samples were passed through Amberlite IR120 resin to remove the chance of metals such as lead precipitating in the column eluent; furthermore, samples were all pre-filtered through a 0.45µm filter. Pre-treatment of samples with a SEP-PAK $C_{18}$ cartridge can also remove organic molecules that might interfere with column efficiency and cause baseline drifting e.g. ghost peaks.

**Table 5.1 Peak Area and Peak Height Measurements for Anions Taken a Week Apart**

| Weight of Anion (ng) | | Peak Area Units | Peak Height (nm) | Retention Time (mins) | Peak Area Units | Peak Height (nm) | Retention Time (mins) |
|---|---|---|---|---|---|---|---|
| $HPO_4^{2-}$ | 200 | 623 | 13 | 2.83 | 350 | 9 | 2.75 |
| | 400 | 2090 | 28 | 2.91 | 1286 | 20 | 2.75 |
| | 600 | 3143 | 42 | 2.85 | 2327 | 34 | 2.75 |
| | 800 | 4212 | 56 | 2.85 | 3439 | 46 | 2.75 |
| | 1000 | 5121 | 69 | 2.87 | 4052 | 53 | 2.75 |
| $Cl^-$ | 50 | 1133 | 34 | 3.31 | 1240 | 37 | 3.11 |
| | 120 | 2575 | 67 | 3.41 | 2534 | 72 | 3.11 |
| | 160 | 3517 | 88 | 3.37 | 3487 | 93 | 3.12 |
| | 200 | 4260 | 110 | 3.35 | 4539 | 115 | 3.12 |
| | 240 | 5137 | 132 | 3.38 | 5216 | 141 | 3.12 |
| $NO_3^-$ | 50 | 600 | 10 | 6.58 | 570 | 10 | 5.85 |
| | 120 | 1399 | 20 | 6.77 | 1168 | 20 | 5.85 |
| | 160 | 1630 | 25 | 6.69 | 1585 | 27 | 5.83 |
| | 200 | 2166 | 32 | 6.65 | 2060 | 32 | 5.81 |
| | 240 | 2549 | 37 | 6.68 | 2461 | 39 | 5.28 |
| $SO_4^{2-}$ | 200 | 1980 | 14 | 12.58 | 1934 | 13 | 12.05 |
| | 400 | 4130 | 32 | 13.13 | 3775 | 29 | 12.07 |
| | 600 | 6041 | 43 | 12.95 | 6616 | 45 | 12.06 |
| | 800 | 8000 | 57 | 12.95 | 8534 | 59 | 12.07 |
| | 1000 | 10110 | 71 | 13.01 | 10229 | 70 | 12.06 |

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## Appendix C1a

### Haw total heavy metal concentrations

Data collected from concentrated nitric acid digests: mean values in bold; data in parentheses are ± standard errors. n=3 (replicates).

| Soil depth (cm) | Cadmium (mg/kg) | Copper (mg/kg) | Lead (mg/kg) | Zinc (mg/kg) |
|---|---|---|---|---|
| L | **18.72** (0.19) | **110.7** (0.4) | **924** (16.1) | **1309** ( 6.5) |
| F | **51.56** (0.33) | **235.8** (1.4) | **2341** (16.8) | **3009** (28.7) |
| H | **73.37** (0.53) | **173.7** (1.4) | **3184** (65.7) | **3388** (18.5) |
| 0-1 | **33.79** (0.06) | **45.2** (0.2) | **460** ( 1.7) | **1690** ( 1.5) |
| 1-3.5 | **20.02** (0.25) | **32.8** (0.4) | **147** ( 2.0) | **1234** ( 4.5) |
| 3.5-6 | **11.17** (0.12) | **33.0** (0.2) | **120** ( 1.4) | **848** (12.6) |
| 6-8.5 | **5.25** (0.06) | **30.4** (0.6) | **168** (56.2) | **478** ( 3.2) |
| 8.5-11 | **2.75** (0.05) | **28.0** (0.4) | **61** ( 0.8) | **333** ( 2.8) |
| 11-13.5 | **2.00** (0.05) | **26.6** (0.3) | **52** ( 0.3) | **262** ( 4.6) |
| 13.5-16 | **1.48** (0.05) | **26.1** (0.8) | **46** ( 2.3) | **194** ( 6.2) |
| 16-18.5 | **1.30** (0.08) | **26.4** (0.3) | **41** ( 0.5) | **154** ( 3.0) |
| 18.5-21 | **1.12** (0.08) | **26.9** (0.4) | **38** ( 0.6) | **144** ( 2.5) |
| 21-23.5 | **1.25** (0.05) | **27.5** (0.7) | **37** ( 0.8) | **140** ( 2.6) |
| 23.5-26 | **0.97** (0.05) | **27.9** (0.2) | **34** ( 0.9) | **117** ( 1.5) |
| 26-28.5 | **0.73** (0.03) | **29.4** (0.1) | **31** ( 0.7) | **107** ( 1.5) |
| 28.5-31 | **0.78** (0.06) | **30.4** (0.03) | **56** ( 1.3) | **115** ( 0.9) |
| 31-33.5 | **0.67** (0.06) | **30.4** (0.8) | **26** ( 0.8) | **102** ( 1.4) |
| 33.5-36 | **0.58** (0.08) | **29.9** (0.1) | **23** ( 0.7) | **89** ( 0.4) |
| 36-38.5 | **0.48** (0.08) | **30.0** (0.3) | **19** ( 0.6) | **56** ( 1.0) |
| 38.5-41 | **0.23** (0.05) | **30.3** (0.3) | **21** ( 0.7) | **48** ( 0.3) |
| 41-46 | **0.27** (0.05) | **29.6** (0.4) | **21** ( 0.3) | **42** ( 0.5) |

## Appendix C1a (cont.)

| Soil depth (cm) | Manganese (mg/kg) | Iron (mg/kg) | Aluminium (mg/kg) | Potassium (mg/kg) | Calcium (mg/kg) |
|---|---|---|---|---|---|
| L | 121 | 2030 | 1261 | 2357 | 19316 |
| F | 392 | 7664 | 5199 | 2468 | 21042 |
| H | 584 | 12669 | 7178 | 3158 | 17674 |
| 0-1 | 917 | 27561 | 13703 | 5397 | 8673 |
| 1-3.5 | 909 | 28304 | 14365 | 5836 | 7527 |
| 3.5-6 | 868 | 28573 | 13951 | 5233 | 7698 |
| 6-8.5 | 985 | 29918 | 15071 | 6082 | 7548 |
| 8.5-11 | 874 | 31040 | 15492 | 5355 | 7227 |
| 11-13.5 | 881 | 30523 | 15584 | 5770 | 7053 |
| 13.5-16 | 975 | 30108 | 15356 | 5660 | 6660 |
| 16-18.5 | 1210 | 30590 | 15695 | 5681 | 6509 |
| 18.5-21 | 1141 | 30768 | 16474 | 6412 | 6610 |
| 21-23.5 | 1157 | 30983 | 16055 | 6062 | 6551 |
| 23.5-26 | 1171 | 31402 | 17915 | 7038 | 6693 |
| 26-28.5 | 1004 | 30320 | 16823 | 6833 | 7002 |
| 28.5-31 | 857 | 29854 | 16894 | 7502 | 6736 |
| 31-33.5 | 730 | 29874 | 16248 | 9270 | 6731 |
| 33.5-36 | 644 | 29087 | 16001 | 7523 | 6464 |
| 36-38.5 | 897 | 29706 | 13988 | 6607 | 5996 |
| 38.5-41 | 765 | 27266 | 14412 | 6065 | 5822 |
| 41-46 | 746 | 28836 | 13048 | 5920 | 6063 |

## Appendix C 1a (cont.)

### Soil environmental variables

| Soil depth (cm) | Soil pH | % Loss-on-Ignition | Bulk Density | Cation-Exchange-Capacity | % Base Saturation |
|---|---|---|---|---|---|
| L | 6.4 | 89.9 | 0.18 | 25.1 | 52.6 |
| F | 5.0 | 73.3 | 0.22 | 27.9 | 50.4 |
| H | 4.9 | 60.2 | 0.26 | 31.2 | 37.3 |
| 0-1 | 5.2 | 14.4 | 0.73 | 16.9 | 49.4 |
| 1-3.5 | 5.3 | 10.1 | 0.89 | 16.1 | 53.4 |
| 3.5-6 | 5.7 | 9.9 | 0.90 | 13.2 | 56.7 |
| 6-8.5 | 5.9 | 8.5 | 0.96 | 13.0 | 59.3 |
| 8.5-11 | 6.0 | 6.8 | 1.06 | 12.5 | 61.4 |
| 11-13.5 | 5.9 | 6.3 | 1.09 | 12.3 | 60.1 |
| 13.5-16 | 5.9 | 6.0 | 1.11 | 12.5 | 61.4 |
| 16-18.5 | 5.3 | 5.5 | 1.15 | 11.9 | 55.6 |
| 18.5-21 | 5.3 | 5.3 | 1.17 | 11.7 | 54.7 |
| 21-23.5 | 5.8 | 5.4 | 1.16 | 11.4 | 53.9 |
| 23.5-26 | 5.6 | 5.1 | 1.18 | 11.2 | 56.9 |
| 26-28.5 | 5.7 | 4.7 | 1.21 | 10.8 | 57.1 |
| 28.5-31 | 5.9 | 4.3 | 1.25 | 9.2 | 59.5 |
| 31-33.5 | 6.0 | 3.9 | 1.28 | 8.8 | 62.5 |
| 33.5-36 | 6.0 | 3.7 | 1.30 | 8.1 | 64.9 |
| 36-38.5 | 6.2 | 3.2 | 1.34 | 6.6 | 76.7 |
| 38.5-41 | 6.3 | 3.0 | 1.36 | 6.4 | 82.8 |
| 41-46 | 6.4 | 2.7 | 1.39 | 6.4 | 86.2 |

## Appendix C1b

### Hallen total heavy metal concentrations

Data collected from concentrated nitric acid digests: mean values in bold; data in parentheses are ± standard errors. n=3 (replicates)

| Soil depth cm | Cadmium (mg/kg) | Copper (mg/kg) | Lead (mg/kg) | Zinc (mg/kg) |
|---|---|---|---|---|
| L | **28.62** (0.22) | **268.2** (2.0) | **2172** ( 1.7) | **1889** (11.7) |
| F | **33.21** (0.71) | **196.9** (6.0) | **4798** (840) | **1864** (13.0) |
| H | **37.20** (0.57) | **165.1** (2.2) | **4052** (24.6) | **1714** (14.8) |
| 0-1 | **10.47** (0.04) | **43.9** (0.3) | **738** (1.7) | **613** ( 1.1) |
| 1-3.5 | **4.60** (0.10) | **23.6** (0.2) | **195** (0.5) | **334** ( 0.2) |
| 3.5-6 | **4.27** (0.04) | **21.9** (0.1) | **132** (1.4) | **306** ( 1.2) |
| 6-8.5 | **4.12** (0.06) | **19.8** (0.1) | **83** (0.6) | **291** ( 1.0) |
| 8.5-11 | **4.88** (0.06) | **20.4** (0.4) | **67** (0.7) | **318** ( 0.7) |
| 11-13.5 | **5.05** (0.05) | **19.2** (<0.05) | **62** (0.8) | **339** ( 1.1) |
| 13.5-16 | **5.47** (0.04) | **19.9** (0.1) | **57** (1.2) | **364** ( 1.6) |
| 16-18.5 | **5.83** (0.04) | **20.8** (0.1) | **49** (0.6) | **388** ( 4.2) |
| 18.5-21 | **5.92** (0.16 | **21.0** (0.2) | **48** (0.6) | **402** ( 2.2) |
| 21-23.5 | **6.50** (0.10 | **22.5** 0.7) | **44** (0.7) | **450** ( 8.5) |
| 23.5-26 | **6.60** (0.03 | **23.0** 0.2) | **42** (0.4) | **458** ( 1.8) |
| 26-28.5 | **6.78** (0.02 | **24.3** 0.1) | **39** (0.7) | **462** ( 0.6) |
| 28 5-31 | **6.08** (0.37 | **25.0** 1.4) | **38** (2.7) | **452** (22.9) |
| 31-33.5 | **6.10** (0.16 | **27.3** 0.8) | **46** (1.0) | **480** (10.1) |
| 33 5-36 | **5.77** (0.09) | **29.6** (0.2) | **47** (0.8) | **479** ( 1.2) |
| 36-38.5 | **5.45** (0.08) | **29.0** (0.2) | **45** (0.5) | **449** ( 4.4) |
| 38.5-41 | **5.37** (0.08) | **33.1** (2.5) | **49** (3.2) | **457** (30.5) |
| 41-43.5 | **4.03** (0.44) | **31.3** (0.3) | **38** (0.8) | **404** ( 2.6) |
| 43.5-46 | **3.42** (0.09) | **31.1** (0.3) | **37** (0.5) | **370** ( 2.2) |
| 46-48.5 | **2.98** (0.07) | **31.3** (0.4) | **48** (1.5) | **329** ( 3.5) |
| 48.5-51 | **2.43** (0.08) | **30.7** (0.6) | **46** (0.8) | **249** ( 3.0) |
| 51-53.5 | **2.20** (0.10) | **31.9** (0.4) | **31** (0.6) | **178** ( 3.3) |
| 53 5-56 | **1.48** (0.13) | **34.6** (0.3) | **22** (0.7) | **142** ( 2.0) |
| 56-58.5 | **0.83** (0.03) | **36.4** (0.2) | **16** (0.6) | **112** ( 1.2) |
| 58.5-61 | **0.38** (0.04) | **33.9** (0.2) | **16** (0.7) | **101** ( 1.4) |
| 61-63.5 | **0.28** (0.04) | **32.1** (0.7) | **15** (0.7) | **100** ( 2.8) |
| 63 5-66 | **0.28** (0.07) | **31.9** (0.2) | **14** (0.3) | **97** ( 0.4) |
| 66-68.5 | **0.03** (0.02) | **30.9** (0.4) | **13** (0.3) | **83** ( 1.0) |
| 68.5-71 | **0.00** <0.01 | **31.2** (0.3) | **13** (<0.05) | **72** ( 0.7) |
| 71-73.5 | **0.05** <0.01 | **29.9** (0.5) | **13** (0.4) | **74** ( 0.4) |
| 73.5-78 | **0.00** <0.01 | **31.8** (0.2) | **15** (0.5) | **74** ( 0.5) |
| 78-83.5 | **0.00** <0.01 | **32.6** (0.2) | **14** (0.3) | **74** ( 1.9) |

## Appendix C1b (cont.)

| Soil depth (cm) | Manganese (mg/kg) | Iron (mg/kg) | Aluminium (mg/kg) | Potassium (mg/kg) | Calcium (mg/kg) |
|---|---|---|---|---|---|
| L | 338 | 4532 | 575 | 3188 | 8782 |
| F | 338 | 12003 | 1567 | 1717 | 4561 |
| H | 382 | 14245 | 2883 | 2057 | 4088 |
| 0-1 | 741 | 25410 | 6450 | 4060 | 1154 |
| 1-3.5 | 679 | 26730 | 8167 | 4698 | 718 |
| 3.5-6 | 656 | 26635 | 7200 | 4392 | 584 |
| 6-8.5 | 604 | 27163 | 7750 | 4293 | 508 |
| 8.5-11 | 676 | 27758 | 8075 | 4455 | 599 |
| 11-13.5 | 696 | 27510 | 6950 | 4332 | 642 |
| 13.5-16 | 739 | 28467 | 7750 | 5438 | 602 |
| 16-18.5 | 759 | 28450 | 8183 | 5888 | 693 |
| 18.5-21 | 806 | 28777 | 10466 | 6038 | 729 |
| 21-23.5 | 830 | 29750 | 10667 | 6188 | 921 |
| 23.5-26 | 803 | 29716 | 12367 | 6373 | 1032 |
| 26-28.5 | 810 | 29903 | 13400 | 7017 | 1136 |
| 28.5-31 | 691 | 28868 | 14100 | 7628 | 1275 |
| 31-33.5 | 684 | 30203 | 15484 | 8256 | 1457 |
| 33.5-36 | 661 | 31565 | 17516 | 9333 | 1629 |
| 36-38.5 | 710 | 31978 | 16700 | 8647 | 1763 |
| 38.5-41 | 744 | 35783 | 18033 | 9303 | 2054 |
| 41-43.5 | 600 | 33553 | 17550 | 8503 | 1950 |
| 43.5-46 | 594 | 35568 | 17717 | 8916 | 2166 |
| 46-48.5 | 628 | 35423 | 18600 | 8581 | 2148 |
| 48.5-51 | 600 | 32587 | 16733 | 6605 | 2284 |
| 51-53.5 | 625 | 35473 | 17600 | 7018 | 2451 |
| 53.5-56 | 619 | 37097 | 17934 | 8287 | 2656 |
| 56-58.5 | 607 | 39420 | 19533 | 8105 | 2993 |
| 58.5-61 | 586 | 38877 | 18067 | 7280 | 3319 |
| 61-63.5 | 628 | 37787 | 18400 | 6943 | 4007 |
| 63.5-66 | 715 | 36868 | 19366 | 6932 | 10330 |
| 66-68.5 | 767 | 35420 | 18533 | 6835 | 26180 |
| 68.5-71 | 711 | 34050 | 16817 | 6597 | 31253 |
| 71-73.5 | 688 | 33575 | 16550 | 6121 | 36019 |
| 73.5-78.5 | 691 | 34775 | 16667 | 6320 | 34732 |
| 78.5-83.5 | 691 | 34502 | 16550 | 6188 | 38906 |

## Appendix C 1b (cont.)

### Soil environmental variables

| Soil depth (cm) | Soil pH | % Loss-on-Ignition | Bulk Density | Cation-Exchange-Capacity | % Base Saturation |
|---|---|---|---|---|---|
| L | 4.1 | 84.1 | 0.19 | 34.3 | 37.2 |
| F | 3.9 | 63.3 | 0.24 | 31.0 | 23.4 |
| H | 4.0 | 51.9 | 0.29 | 29.3 | 24.1 |
| 0-1 | 4.4 | 11.3 | 0.84 | 18.3 | 22.9 |
| 1-3.5 | 4.6 | 6.7 | 1.07 | 16.7 | 22.4 |
| 3.5-6 | 4.4 | 6.2 | 1.10 | 16.5 | 25.3 |
| 6-8.5 | 4.6 | 5.4 | 1.16 | 16.7 | 26.3 |
| 8.5-11 | 4.5 | 5.2 | 1.17 | 16.1 | 26.0 |
| 11-13.5 | 4.6 | 5.0 | 1.19 | 15.4 | 24.3 |
| 13.5-16 | 4.7 | 5.0 | 1.19 | 15.6 | 28.2 |
| 16-18.5 | 4.7 | 4.7 | 1.21 | 15.2 | 27.5 |
| 18.5-21 | 4.8 | 4.7 | 1.21 | 15.6 | 28.2 |
| 21-23.5 | 4.8 | 4.6 | 1.22 | 15.2 | 31.9 |
| 23.5-26 | 4.9 | 5.3 | 1.17 | 14.7 | 34.3 |
| 26-28.5 | 4.9 | 5.5 | 1.15 | 14.7 | 34.3 |
| 28.5-31 | 5.1 | 5.7 | 1.14 | 13.9 | 34.9 |
| 31-33.5 | 5.0 | 5.7 | 1.14 | 14.7 | 41.8 |
| 33.5-36 | 5.1 | 5.7 | 1.14 | 14.7 | 47.8 |
| 36-38.5 | 5.1 | 5.7 | 1.13 | 15.0 | 50.0 |
| 38.5-41 | 5.2 | 5.9 | 1.12 | 14.5 | 50.0 |
| 41-43.5 | 5.2 | 5.9 | 1.12 | 15.0 | 51.4 |
| 43.5-46 | 5.3 | 5.7 | 1.14 | 15.0 | 51.5 |
| 46-48.5 | 5.5 | 4.4 | 1.24 | 15.0 | 50.0 |
| 48.5-51 | 5.4 | 3.8 | 1.29 | 13.6 | 50.0 |
| 51-53.5 | 6.0 | 3.3 | 1.34 | 14.1 | 59.4 |
| 53.5-56 | 6.4 | 2.9 | 1.38 | 12.3 | 66.1 |
| 56-58.5 | 6.7 | 2.6 | 1.41 | 10.3 | 74.5 |
| 58.5-61 | 7.3 | 2.6 | 1.42 | 10.1 | 86 9 |
| 61-63.5 | 7.8 | 2.3 | 1.44 | 10.8 | 93 9 |
| 63.5-66 | 8.3 | 2.1 | 1.47 | 19.4 | 100 |
| 66-68.5 | 7.8 | 1.7 | 1.51 | 27.7 | 100 |
| 68.5-71 | 8.2 | 1.7 | 1.52 | 30.6 | 100 |
| 71-73.5 | 8.0 | 1.5 | 1.54 | 32.3 | 100 |
| 73.5-78.5 | 8.0 | 1.5 | 1.54 | 31.7 | 100 |
| 78.5-83.5 | 8.2 | 1.5 | 1.54 | 32.7 | 100 |

## Appendix C 2a

### Haw sequential extraction results

Data collected from five different chemical extractants ($H_2O$, 0.1M $NH_4NO_3$, 0.1M $CaCl_2$, 2.5% $CH_3COOH$ and 0.2M NaOH) : mean values in bold are metal concentrations found in the Haw soil; data in parentheses are ± standard errors. n=3 (replicates)

Cadmium results (mg/kg)

| Soil depth (cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **0.013** (0.003) | **0.036** (0.003) | **0.555** (0.027) | **0.565** (0.021) | **0.034** (0.007) | **1.203** |
| F | **0.026** (0.005) | **0.076** (0.005) | **1.766** (0.051) | **2.206** (0.154) | **0.086** (0.003) | **4.160** |
| H | **0.050** (0.001) | **0.271** (0.017) | **4.343** (0.274) | **2.831** (0.250) | **0.179** (0.034) | **7.674** |
| 0-1 | **0.026** (0.005) | **0.533** (0.011) | **3.270** (0.080) | **2.789** (0.157) | **0.028** (0.003) | **6.646** |
| 1-3.5 | **0.019** (0.005) | **0.411** (0.021) | **1.811** (0.117) | **1.618** (0.069) | **0.019** (0.007) | **3.878** |
| 3.5-6 | **0.015** (0.004) | **0.214** (0.009) | **0.984** (0.130) | **1.005** (0.053) | **0.018** (0.003) | **2.236** |
| 6-8.5 | **0.006** (0.001) | **0.106** (0.005) | **0.445** (0.028) | **0.594** (0.016) | **0.010** (0.002) | **1.161** |
| 8.5-11 | **0.003** (0.001) | **0.055** (0.006) | **0.310** (0.024) | **0.266** (0.027) | **0.001** (0.001) | **0.635** |
| 11-13.5 | **0.005** <0.001 | **0.049** (0.007) | **0.176** (0.011) | **0.199** (0.008) | **0.004** (0.001) | **0.433** |
| 13.5-16 | **0.003** <0.001 | **0.030** (0.003) | **0.160** (0.033) | **0.165** (0.018) | **0.003** (0.001) | **0.361** |
| 16-18.5 | **0.005** (0.002) | **0.024** (0.003) | **0.099** (0.011) | **0.134** (0.005) | **0.001** <0.001 | **0.263** |
| 18.5-21 | **0.005** (0.002) | **0.028** (0.002) | **0.083** (0.006) | **0.121** (0.005) | **0.003** (0.001) | **0.240** |
| 21-23.5 | **0.005** (0.002) | **0.025** (0.004) | **0.100** (0.006) | **0.131** (0.017) | **0.005** (0.001) | **0.266** |
| 23.5-26 | **0.006** (0.001) | **0.019** (0.002) | **0.093** (0.008) | **0.088** (0.007) | **0.004** (0.001) | **0.210** |
| 26-28.5 | **0.009** (0.001) | **0.022** (0.002) | **0.070** (0.004) | **0.075** (0.004) | **0.005** (0.002) | **0.181** |
| 28.5-31 | **0.007** (0.002) | **0.017** (0.004) | **0.065** (0.006) | **0.106** (0.007) | **0.002** <0.001 | **0.197** |
| 31-33.5 | **0.006** (0.002) | **0.011** (0.001) | **0.073** (0.008) | **0.086** (0.003) | **<0.001** | **0.176** |
| 33.5-36 | **0.004** (0.001) | **0.005** (0.001) | **0.051** (0.007) | **0.079** (0.009) | **<0.001** | **0.139** |
| 36-38.5 | **0.002** <0.001 | **0.003** (0.001) | **0.039** (0.007) | **0.045** (0.004) | **<0.001** | **0.089** |
| 38.5-41 | **0.001** <0.001 | **0.002** (0.001) | **0.025** (0.003) | **0.025** (0.002) | **<0.001** | **0.053** |
| 41-46 | **0.001** <0.001 | **0.001** <0.001 | **0.024** (0.004) | **0.021** (0.003) | **<0.001** | **0.047** |

**Appendix C 2a (cont.)**

Copper results (mg/kg)

| Soil depth cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **0.228** (0.035) | **0.129** (0.003) | **0.100** (0.007) | **0.144** (0.011) | **0.216** (0.005) | **0.817** |
| F | **0.171** (0.005) | **0.070** (0.005) | **0.058** (0.005) | **0.146** (0.009) | **1.005** (0.043) | **1.450** |
| H | **0.131** (0.015) | **0.048** (0.003) | **0.060** (0.006) | **0.123** (0.012) | **1.118** (0.074) | **1.480** |
| 0-1 | **0.048** (0.004) | **0.058** (0.002) | **0.055** (0.004) | **0.121** (0.005) | **0.304** (0.005) | **0.586** |
| 1-3.5 | **0.035** (0.003) | **0.056** (0.002) | **0.071** (0.005) | **0.106** (0.008) | **0.305** (0.041) | **0.573** |
| 3.5-6 | **0.050** (0.002) | **0.054** (0.005) | **0.065** (0.007) | **0.123** (0.008) | **0.470** (0.021) | **0.762** |
| 6-8.5 | **0.020** (0.002) | **0.043** (0.004) | **0.073** (0.005) | **0.135** (0.008) | **0.462** (0.013) | **0.733** |
| 8.5-11 | **0.024** (0.003) | **0.039** (0.002) | **0.060** (0.005) | **0.141** (0.005) | **0.280** (0.014) | **0.544** |
| 11-13.5 | **0.027** (0.003) | **0.040** (0.006) | **0.074** (0.004) | **0.145** (0.007) | **0.322** (0.010) | **0.608** |
| 13.5-16 | **0.033** (0.003) | **0.034** (0.002) | **0.060** (0.003) | **0.150** (0.011) | **0.269** (0.021) | **0.546** |
| 16-18.5 | **0.024** (0.002) | **0.029** (0.003) | **0.066** (0.004) | **0.146** (0.006) | **0.184** (0.009) | **0.449** |
| 18.5-21 | **0.020** (0.002) | **0.030** (0.002) | **0.078** (0.008) | **0.145** (0.008) | **0.214** (0.007) | **0.487** |
| 21-23.5 | **0.031** (0.003) | **0.034** (0.002) | **0.080** (0.006) | **0.142** (0.009) | **0.231** (0.016) | **0.518** |
| 23.5-26 | **0.018** (0.002) | **0.050** (0.004) | **0.096** (0.006) | **0.141** (0.010) | **0.195** (0.011) | **0.500** |
| 26-28.5 | **0.026** (0.002) | **0.041** (0.006) | **0.089** (0.008) | **0.129** (0.005) | **0.129** (0.007) | **0.414** |
| 28.5-31 | **0.010** (0.002) | **0.029** (0.003) | **0.076** (0.004) | **0.154** (0.011) | **0.130** (0.008) | **0.399** |
| 31-33.5 | **0.008** (0.001) | **0.044** (0.004) | **0.079** (0.003) | **0.136** (0.007) | **0.091** (0.006) | **0.358** |
| 33.5-36 | **0.007** (0.001) | **0.036** (0.003) | **0.071** (0.005) | **0.125** (0.009) | **0.093** (0.005) | **0.332** |
| 36-38.5 | **0.007** (0.002) | **0.026** (0.003) | **0.074** (0.007) | **0.115** (0.005) | **0.054** (0.003) | **0.276** |
| 38.5-41 | **0.006** (0.001) | **0.021** (0.002) | **0.069** (0.005) | **0.110** (0.006) | **0.056** (0.004) | **0.262** |
| 41-46 | **0.003** <0.001 | **0.017** (0.002) | **0.072** (0.005) | **0.103** (0.005) | **0.049** (0.004) | **0.244** |

**Appendix C 2a (cont.)**

Lead results (mg/kg)

| Soil depth cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **0.48** (0.06) | **0.23** (0.02) | **1.93** (0.06) | **3.31** (0.24) | **0.91** (0.09) | **6.86** |
| F | **0.40** (0.04) | **0.27** (0.03) | **6.84** (0.46) | **1.08** (0.06) | **2.04** (0.15) | **10.63** |
| H | **0.60** (0.08) | **0.31** (0.02) | **7.68** (0.32) | **3.25** (0.18) | **4.46** (0.36) | **16.30** |
| 0-1 | **0.06** (0.02) | **0.05** (0.02) | **1.99** (0.11) | **1.68** (0.11) | **0.03** (0.01) | **3.76** |
| 1-3.5 | **0.04** (0.01) | **0.03** (0.01) | **0.34** (0.02) | **0.31** (0.05) | **0.03** (0.01) | **0.75** |
| 3.5-6 | **0.03** (0.01) | **0.06** (0.02) | **0.25** (0.04) | **0.38** (0.02) | **0.03** (0.01) | **0.74** |
| 6-8.5 | **0.02** (0.01) | **0.10** (0.03) | **2.06** (0.13) | **1.55** (0.16) | **0.01** (0.01) | **3.74** |
| 8.5-11 | **0.01** (0.01) | **0.08** (0.02) | **0.21** (0.02) | **0.39** (0.02) | **0.01** (0.01) | **0.70** |
| 11-13.5 | **0.01** <0.01 | **0.10** (0.03) | **0.13** (0.02) | **0.30** (0.02) | **0.04** (0.02) | **0.58** |
| 13.5-16 | **0.01** <0.01 | **0.05** (0.02) | **0.16** (0.02) | **0.31** (0.03) | **0.03** (0.01) | **0.56** |
| 16-18.5 | **<0.01** | **0.06** (0.01) | **0.16** (0.03) | **0.40** (0.03) | **0.01** (0.01) | **0.63** |
| 18.5-21 | **<0.01** | **0.09** (0.02) | **0.11** (0.02) | **0.37** (0.03) | **0.02** (0.01) | **0.59** |
| 21-23.5 | **<0.01** | **0.11** (0.03) | **0.14** (0.02) | **0.42** (0.02) | **0.01** <0.01 | **0.68** |
| 23.5-26 | **<0.01** | **0.05** (0.02) | **0.16** (0.01) | **0.36** (0.03) | **<0.01** | **0.57** |
| 26-28.5 | **<0.01** | **0.02** (0.01) | **0.24** (0.03) | **0.33** (0.02) | **<0.01** | **0.59** |
| 28.5-31 | **<0.01** | **0.01** (0.01) | **0.33** (0.03) | **0.50** (0.04 | **<0.01** | **0.84** |
| 31-33.5 | **<0.01** | **0.01** (0.01) | **0.10** (0.02) | **0.10** (0.02) | **<0.01** | **0.16** |
| 33.5-36 | **<0.01** | **0.01** <0.01 | **0.04** (0.02) | **0.04** (0.02) | **<0.01** | **0.08** |
| 36-38.5 | **<0.01** | **<0.01** | **0.02** (0.01) | **0.02** (0.01) | **<0.01** | **0.03** |
| 38.5-41 | **<0.01** | **<0.01** | **0.01** (0.01) | **0.01** (0.01) | **<0.01** | **0.02** |
| 41-46 | **<0.01** | **<0.01** | **0.01** <0.01 | **0.01** (0.01) | **<0.01** | **0.02** |

## Appendix C 2a (cont.)

Zinc results (mg/kg)

| Soil depth cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **1.960** (0.128) | **2.855** (0.245) | **19.610** (1.613) | **27.551** (1.498) | **1.541** (0.137) | **53.517** |
| F | **2.709** (0.095) | **6.641** (0.148) | **47.138** (0.684) | **89.113** (3.583) | **2.570** (0.154) | **148.171** |
| H | **3.994** (0.179) | **20.175** (1.225) | **116.925** (5.51) | **102.212** (6.338) | **4.321** (0.395) | **247.627** |
| 0-1 | **1.688** (0.121) | **40.983** (0.901) | **93.050** (1.768) | **95.625** (2.388) | **0.225** (0.017) | **231.571** |
| 1-3.5 | **1.225** (0.073) | **34.970** (1.368) | **60.507** (2.939) | **66.575** (1.837) | **0.253** (0.020) | **163.530** |
| 3.5-6 | **1.107** (0.020) | **22.871** (0.849) | **38.352** (3.479) | **50.524** (1.634) | **0.139** (0.009) | **112.993** |
| 6-8.5 | **0.418** (0.044) | **10.200** (0.636) | **15.525** (0.776) | **30.063** (0.337) | **0.078** (0.006) | **56.284** |
| 8.5-11 | **0.238** (0.017) | **4.962** (0.451) | **9.314** (0.469) | **12.662** (1.133) | **0.091** (0.007) | **27.267** |
| 11-13.5 | **0.135** (0.007) | **3.151** (0.181) | **4.573** (0.232) | **8.263** (0.230) | **0.161** (0.028) | **16.283** |
| 13.5-16 | **0.146** (0.008) | **1.865** (0.064) | **3.109** (0.273) | **5.244** (0.713) | **0.018** (0.004) | **10.382** |
| 16-18.5 | **0.161** (0.011) | **1.086** (0.047) | **1.723** (0.100) | **3.365** (0.102) | **0.010** (0.002) | **6.345** |
| 18.5-21 | **0.100** (0.005) | **0.896** (0.038) | **1.506** (0.113) | **2.828** (0.141) | **0.037** (0.004) | **5.367** |
| 21-23.5 | **0.147** (0.007) | **0.790** (0.035) | **1.623** (0.049) | **2.936** (0.0960 | **0.031** (0.002) | **5.527** |
| 23.5-26 | **0.122** (0.012) | **0.559** (0.052) | **1.138** (0.067) | **1.882** (0.126) | **0.034** (0.003) | **3.735** |
| 26-28.5 | **0.107** (0.008) | **0.254** (0.013) | **0.633** (0.014) | **1.392** (0.059) | **0.048** (0.004) | **2.434** |
| 28.5-31 | **0.121** (0.006) | **0.235** (0.017) | **0.579** (0.024) | **1.806** (0.084) | **0.005** (0.002) | **2.746** |
| 31-33.5 | **0.079** (0.004) | **0.151** (0.009) | **0.498** (0.031) | **1.397** (0.066) | **0.022** (0.004) | **2.147** |
| 33.5-36 | **0.063** (0.005) | **0.095** (0.006) | **0.314** (0.022) | **1.081** (0.031) | **0.011** (0.002) | **1.564** |
| 36-38.5 | **0.042** (0.003) | **0.071** (0.005) | **0.269** (0.017) | **0.549** (0.025) | **0.010** (0.002) | **0.941** |
| 38.5-41 | **0.036** (0.004) | **0.065** (0.005) | **0.158** (0.010) | **0.345** (0.027) | **0.008** (0.001) | **0.612** |
| 41-46 | **0.030** (0.003) | **0.064** (0.004) | **0.181** (0.012) | **0.201** (0.014) | **0.006** (0.001) | **0.482** |

## Appendix C 2a (cont.)

### Haw exchangeable metals and acidity

Data collected from the sum of two different chemical extractants ($H_2O$ and $NH_4NO_3$): mean values in bold are EXCH concentrations in the Haw soil. n=3 (replicates).

| Soil depth (cm) | Concentrations (meq/100g) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Al^{3+}$ | $Mn^{2+}$ | $Fe^{2+}$ | Acidity |
| L | **0.387** | **0.126** | **0.212** | **0.538** | **0.002** | **0.001** | **0.001** | **0.054** |
| F | **0.579** | **0.128** | **0.209** | **0.405** | **0.004** | **0.002** | **0.001** | **0.308** |
| H | **0.685** | **0.121** | **0.210** | **0.365** | **0.004** | **0.004** | **0.002** | **0.629** |
| 0-1 | **1.267** | **0.216** | **0.173** | **0.568** | **0.003** | **0.008** | **0.002** | **0.186** |
| 1-3.5 | **1.265** | **0.200** | **0.134** | **0.490** | **0.002** | **0.006** | **0.001** | **0.158** |
| 3.5-6 | **1.318** | **0.198** | **0.137** | **0.474** | **0.003** | **0.007** | **0.002** | **0.095** |
| 6-8.5 | **1.410** | **0.197** | **0.130** | **0.377** | **0.002** | **0.007** | **0.001** | **0.085** |
| 8.5-11 | **1.393** | **0.191** | **0.132** | **0.287** | **0.002** | **0.007** | **0.001** | **0.074** |
| 11-13.5 | **1.592** | **0.211** | **0.148** | **0.299** | **0.003** | **0.006** | **0.001** | **0.083** |
| 13.5-16 | **1.428** | **0.185** | **0.139** | **0.266** | **0.003** | **0.005** | **0.001** | **0.093** |
| 16-18.5 | **1.336** | **0.173** | **0.133** | **0.253** | **0.003** | **0.005** | **0.001** | **0.102** |
| 18.5-21 | **1.341** | **0.174** | **0.131** | **0.256** | **0.002** | **0.006** | **0.002** | **0.099** |
| 21-23.5 | **1.294** | **0.167** | **0.137** | **0.282** | **0.001** | **0.004** | **0.001** | **0.076** |
| 23.5-26 | **1.444** | **0.181** | **0.145** | **0.271** | **0.002** | **0.005** | **0.001** | **0.081** |
| 26-28.5 | **1.224** | **0.148** | **0.133** | **0.211** | **0.002** | **0.003** | **0.001** | **0.071** |
| 28.5-31 | **1.344** | **0.163** | **0.143** | **0.238** | **0.001** | **0.003** | **0.001** | **0.054** |
| 31-33.5 | **1.361** | **0.161** | **0.146** | **0.233** | **0.001** | **0.003** | **0.001** | **0.041** |
| 33.5-36 | **1.133** | **0.127** | **0.128** | **0.180** | **0.001** | **0.002** | **0.002** | **0.033** |
| 36-38.5 | **1.136** | **0.120** | **0.124** | **0.170** | **0.001** | **0.002** | **0.003** | **0.027** |
| 38.5-41 | **1.262** | **0.128** | **0.134** | **0.164** | **0.001** | **0.001** | **0.003** | **0.024** |
| 41-46 | **1.223** | **0.116** | **0.139** | **0.137** | **0.001** | **0.001** | **0.003** | **0.020** |

## Appendix C 2b

### Hallen sequential extraction results

Data collected from five different chemical extractants ($H_2O$, 0.1M $NH_4NO_3$, 0.1M $CaCl_2$, 2.5% $CH_3COOH$ and 0.2M NaOH) : mean values in bold are metal concentrations found in the Hallen soil; data in parentheses are ± standard errors. n=3 (replicates)

Cadmium results (mg/kg)

| Soil depth (cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **0.078** (0.005) | **0.228** (0.012) | **1.489** (0.046) | **1.245** (0.069) | **0.081** (0.005) | **3.120** |
| F | **0.096** (0.005) | **0.470** (0.014) | **2.486** (0.204) | **1.506** (0.255) | **0.138** (0.018) | **4.696** |
| H | **0.103** (0.008) | **0.615** (0.042) | **2.370** (0.197) | **2.343** (0.185) | **0.130** (0.011) | **5.561** |
| 0-1 | **0.021** (0.002) | **0.776** (0.019) | **1.189** (0.186) | **0.785** (0.004) | **0.028** (0.003) | **2.799** |
| 1-3.5 | **0.023** (0.005) | **0.982** (0.114) | **0.980** (0.087) | **0.588** (0.049) | **0.013** (0.002) | **2.586** |
| 3.5-6 | **0.038** (0.008) | **0.800** (0.180) | **0.811** (0.108) | **0.613** (0.039) | **0.006** (0.002) | **2.268** |
| 6-8.5 | **0.043** (0.007) | **0.952** (0.131) | **1.034** (0.128) | **0.652** (0.040) | **0.005** (0.002) | **2.686** |
| 8.5-11 | **0.028** (0.005) | **1.154** (0.189) | **1.001** (0.093) | **0.806** (0.047) | **0.003** (0.001) | **2.992** |
| 11-13.5 | **0.014** (0.002) | **0.943** (0.118) | **0.990** (0.039) | **0.884** (0.022) | **0.003** (0.001) | **2.834** |
| 13.5-16 | **0.040** (0.001) | **1.318** (0.078) | **1.206** (0.051) | **0.913** (0.070) | **0.005** (0.001) | **3.482** |
| 16-18.5 | **0.037** (0.002) | **1.614** (0.121) | **1.323** (0.059) | **0.904** (0.068) | **0.003** (0.001) | **3.881** |
| 18.5-21 | **0.037** (0.001) | **1.243** (0.064) | **1.418** (0.146) | **1.051** (0.036) | **<0.001** | **3.749** |
| 21-23.5 | **0.039** (0.004) | **1.661** (0.015) | **1.800** (0.051) | **0.834** (0.078) | **<0.001** | **4.334** |
| 23.5-26 | **0.036** (0.002) | **1.622** (0.053) | **1.838** (0.076) | **1.030** (0.067) | **0.005** (0.002) | **4.531** |
| 26-28.5 | **0.032** (0.002) | **1.558** (0.014) | **1.857** (0.078) | **1.107** (0.071) | **0.003** (0.001) | **4.557** |
| 28.5-31 | **0.026** (0.002) | **1.501** (0.050) | **1.762** (0.045) | **1.060** (0.065) | **0.004** (0.001) | **4.353** |
| 31-33.5 | **0.016** (0.002) | **1.373** (0.052) | **1.853** (0.087) | **1.056** (0.026) | **0.007** (0.002) | **4.305** |
| 33.5-36 | **0.013** (0.005) | **1.284** (0.056) | **1.653** (0.058) | **0.948** (0.048) | **0.003** (0.001) | **3.901** |
| 36-38.5 | **0.006** (0.003) | **1.083** (0.012) | **1.403** (0.086) | **0.871** (0.047) | **0.005** (0.002) | **3.368** |
| 38.5-41 | **0.008** (0.004) | **0.922** (0.017) | **1.315** (0.073) | **0.826** (0.063) | **0.002** (0.002) | **3.073** |
| 41-43.5 | **0.004** (0.002) | **0.737** (0.018) | **0.971** (0.107) | **0.649** (0.040) | **0.004** (0.001) | **2.365** |
| 43.5-46 | **0.005** (0.001) | **0.582** (0.032) | **0.867** (0.020) | **0.572** (0.042) | **0.001** (0.001) | **2.027** |
| 46-48.5 | **0.005** (0.001) | **0.456** (0.015) | **0.699** (0.054) | **0.533** (0.035) | **0.002** (0.001) | **1.695** |
| 48.5-51 | **<0.001** | **0.313** (0.008) | **0.550** (0.035) | **0.384** (0.023) | **<0.001** | **1.247** |
| 51-53.5 | **<0.001** | **0.198** (0.010) | **0.387** (0.027) | **0.298** (0.022) | **<0.001** | **0.883** |
| 53.5-56 | **<0.001** | **0.090** (0.003) | **0.264** (0.024) | **0.250** (0.019) | **<0.001** | **0.604** |
| 56-58.5 | **<0.001** | **0.026** (0.002) | **0.107** (0.012) | **0.156** (0.016) | **<0.001** | **0.289** |
| 58.5-61 | **<0.001** | **<0.0001** | **0.044** (0.006) | **0.089** (0.009) | **<0.001** | **0.133** |

**Appendix C 2b(cont.)**

Copper results (mg/kg)

| Soil depth (cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **0.479** (0.012) | **0.453** (0.024) | **0.386** (0.012) | **0.451** (0.018) | **0.950** (0.074) | **2.719** |
| F | **0.353** (0.011) | **0.358** (0.010) | **0.546** (0.018) | **0.537** (0.035) | **1.473** (0.162) | **3.267** |
| H | **0.280** (0.012) | **0.248** (0.031) | **0.385** (0.010) | **0.468** (0.032) | **0.395** (0.025) | **1.776** |
| 0-1 | **0.046** (0.004) | **0.103** (0.004) | **0.260** (0.014) | **0.238** (0.025) | **0.493** (0.038) | **1.140** |
| 1-3.5 | **0.049** (0.004) | **0.118** (0.008) | **0.248** (0.011) | **0.253** (0.013) | **0.445** (0.047) | **1.113** |
| 3.5-6 | **0.063** (0.010) | **0.117** (0.017) | **0.243** (0.024) | **0.278** 0.018) | **0.392** (0.033) | **1.093** |
| 6-8.5 | **0.054** (0.005) | **0.119** (0.010) | **0.259** (0.020) | **0.283** (0.028) | **0.358** (0.041) | **1.073** |
| 8.5-11 | **0.033** (0.006) | **0.113** (0.016) | **0.229** (0.019) | **0.263** (0.010) | **0.326** (0.023) | **0.964** |
| 11-13.5 | **0.030** (0.003) | **0.103** (0.006) | **0.233** (0.003) | **0.268** (0.011) | **0.286** (0.034) | **0.920** |
| 13.5-16 | **0.040** (0.004) | **0.125** (0.004) | **0.246** (0.015) | **0.283** (0.023) | **0.464** (0.028) | **1.158** |
| 16-18.5 | **0.034** (0.002) | **0.141** (0.010) | **0.248** (0.008) | **0.306** (0.021) | **0.458** (0.018) | **1.187** |
| 18.5-21 | **0.028** (0.002) | **0.124** (0.007) | **0.244** (0.007) | **0.297** (0.020) | **0.250** (0.023) | **0.943** |
| 21-23.5 | **0.046** (0.007) | **0.178** (0.006) | **0.248** (0.004) | **0.304** (0.020) | **0.276** (0.018) | **1.052** |
| 23.5-26 | **0.038** (0.002) | **0.182** (0.008) | **0.248** (0.006) | **0.388** (0.027) | **0.367** (0.025) | **1.223** |
| 26-28.5 | **0.038** (0.002) | **0.159** (0.004) | **0.233** (0.012) | **0.384** (0.038) | **0.308** (0.024) | **1.122** |
| 28.5-31 | **0.035** (0.003) | **0.160** (0.009) | **0.223** (0.005) | **0.353** (0.030) | **0.285** (0.033) | **1.056** |
| 31-33.5 | **0.034** (0.004) | **0.142** (0.008) | **0.232** (0.026) | **0.347** (0.027) | **0.266** (0.025) | **1.021** |
| 33.5-36 | **0.026** (0.001) | **0.147** (0.007) | **0.208** (0.011) | **0.317** (0.023) | **0.207** (0.014) | **0.905** |
| 36-38.5 | **0.023** (0.002) | **0.131** (0.004) | **0.180** (0.007) | **0.282** (0.018) | **0.183** (0.011) | **0.799** |
| 38.5-41 | **0.018** (0.005) | **0.111** (0.006) | **0.152** (0.005) | **0.268** (0.022) | **0.187** (0.008) | **0.736** |
| 41-43.5 | **0.011** (0.004) | **0.088** (0.003) | **0.138** (0.004) | **0.219** (0.019) | **0.178** (0.011) | **0.634** |
| 43.5-46 | **0.008** (0.002) | **0.070** (0.005) | **0.098** (0.003) | **0.168** (0.015) | **0.121** (0.010) | **0.465** |
| 46-48.5 | **0.007** (0.005) | **0.057** (0.002) | **0.068** (0.005 | **0.138** (0.008) | **0.101** (0.011) | **0.371** |
| 48.5-51 | **0.012** (0.002) | **0.048** (0.003) | **0.066** (0.001) | **0.094** (0.003) | **0.090** (0.003) | **0.310** |
| 51-53.5 | **0.024** (0.001) | **0.041** (0.005) | **0.054** (0.006) | **0.076** (0.005) | **0.090** (0.011) | **0.285** |
| 53.5-56 | **0.017** (0.003) | **0.031** (0.004) | **0.053** (0.006) | **0.079** (0.004) | **0.077** (0.006) | **0.257** |
| 56-58.5 | **0.004** (0.002) | **0.026** (0.003) | **0.048** (0.005) | **0.073** (0.007) | **0.052** (0.008) | **0.203** |
| 58.5-61 | **0.007** (0.003) | **0.016** (0.006) | **0.043** (0.002) | **0.055** (0.003) | **0.046** (0.007) | **0.167** |

**Appendix C 2b(cont.)**

Lead results (mg/kg)

| Soil depth (cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **1.64** (0.09) | **1.98** (0.10) | **5.86** (0.54) | **7.88** (0.35) | **2.79** (0.12) | **20.15** |
| F | **2.15** (0.10) | **4.25** (0.21) | **30.53** (1.77) | **25.65** (1.51) | **12.94** (1.54) | **75.52** |
| H | **2.33** (0.10) | **4.45** (0.18) | **30.93** (1.54) | **30.00** (2.04) | **6.45** (0.56) | **74.16** |
| 0-1 | **0.16** (0.02) | **4.23** (0.12) | **17.16** (2.03) | **13.98** (0.77) | **0.55** (0.05) | **36.08** |
| 1-3.5 | **0.11** (0.01) | **2.62** (0.13) | **7.08** (0.46) | **7.11** (0.46) | **0.11** (0.03) | **17.02** |
| 3.5-6 | **0.03** (0.01) | **1.13** (0.21) | **2.93** (0.35) | **3.69** (0.33) | **0.06** (0.02) | **7.83** |
| 6-8.5 | **0.02** (0.01) | **0.63** (0.08) | **1.60** (0.22) | **2.00** (0.11) | **0.03** (0.01) | **4.27** |
| 8.5-11 | **0.01** (0.01) | **0.32** (0.05) | **0.71** (0.04) | **1.10** (0.04) | **0.05** (0.02) | **2.18** |
| 11-13.5 | **0.01** (0.01) | **0.22** (0.03) | **0.54** (0.04) | **0.88** (0.07) | **0.01** (0.01) | **1.65** |
| 13.5-16 | **0.03** (0.01) | **0.22** (0.02) | **0.48** (0.03) | **0.80** (0.06) | **0.03** (0.01) | **1.55** |
| 16-18.5 | **0.03** (0.01) | **0.17** (0.02) | **0.38** (0.01) | **0.66** (0.01) | **0.01** (0.01) | **1.23** |
| 18.5-21 | **0.05** (0.02) | **0.09** (0.01) | **0.33** (0.01) | **0.54** (0.02) | **0.03** (0.01) | **1.03** |
| 21-23.5 | **0.02** (0.01) | **0.11** (0.02) | **0.28** (0.02) | **0.56** (0.04) | **0.03** (0.01) | **0.99** |
| 23.5-26 | **0.03** (0.01) | **0.09** (0.01) | **0.21** (0.03) | **0.53** (0.05) | **0.03** (0.01) | **0.88** |
| 26-28.5 | **0.03** (0.02) | **0.07** (0.02) | **0.23** (0.01) | **0.52** (0.06) | **0.03** (0.02) | **0.87** |
| 28.5-31 | **0.03** (0.01) | **0.06** (0.01) | **0.24** (0.03) | **0.54** (0.06) | **0.03** (0.01) | **0.91** |
| 31-33.5 | **0.03** <0.005 | **0.16** (0.01) | **0.34** (0.2) | **0.67** (0.05) | **0.01** (0.01) | **1.20** |
| 33.5-36 | **0.03** (0.01) | **0.07** (0.01) | **0.38** (0.02) | **0.78** (0.04) | **0.04** (0.01) | **1.31** |
| 36-38.5 | **0.02** (0.01) | **0.07** (0.02) | **0.22** (0.02) | **0.60** (0.04) | **0.02** (0.02) | **0.92** |
| 38.5-41 | **0.02** (0.01) | **0.06** (0.03) | **0.22** (0.02) | **0.57** (0.06) | **0.01** <0.005 | **0.86** |
| 41-43.5 | **0.02** (0.01) | **0.07** (0.01) | **0.13** (0.04) | **0.36** (0.01) | **<0.005** | **0.58** |
| 43.5-46 | **0.03** (0.02) | **0.05** (0.02) | **0.16** (0.01) | **0.30** (0.01) | **<0.005** | **0.54** |
| 46-48.5 | **0.01** (0.01) | **0.06** (0.02) | **0.10** (0.01) | **0.43** (0.03) | **<0.005** | **0.59** |
| 48.5-51 | **0.01** (0.01) | **0.05** (0.01) | **0.08** (0.02) | **0.33** (0.02) | **<0.005** | **0.46** |
| 51-53.5 | **<0.005** | **0.03** (0.01) | **0.03** (0.01) | **0.13** (0.01) | **<0.005** | **0.19** |
| 53.5-56 | **<0.005** | **0.03** (0.01) | **0.02** (0.01) | **0.03** (0.01) | **<0.005** | **0.06** |
| 56-58.5 | **<0.005** | **0.02** (0.01) | **0.02** (0.01) | **0.01** (0.01) | **<0.005** | **0.05** |
| 58.5-61 | **<0.005** | **0.01** (0.01) | **0.02** (0.01) | **0.02** (0.01) | **<0.005** | **0.04** |

**Appendix C 2b(cont.)**

Zinc results (mg/kg)

| Soil depth (cm) | $H_2O$ (deionised) | 0.1M $NH_4NO_3$ | 0.1M $CaCl_2$ | 2.5% $CH_3COOH$ | 0.2M NaOH | Sum total extractable |
|---|---|---|---|---|---|---|
| L | **7.308** (0.258) | **17.900** (0.837) | **58.263** (1.219) | **55.288** (4.119) | **2.271** (0.111) | **141.030** |
| F | **7.047** (0.229) | **29.092** (0.956) | **83.125** (4.139) | **54.750** (8.329) | **3.873** (0.229) | **177.887** |
| H | **6.388** (0.195) | **32.900** (1.059) | **72.900** (2.476) | **73.875** (6.522) | **4.360** (0.470) | **190.423** |
| 0-1 | **0.732** (0.041) | **29.833** (0.758) | **32.533** (4.996) | **20.192** (0.837) | **0.176** (0.012) | **83.466** |
| 1-3.5 | **1.243** (0.146) | **35.058** (3.941) | **25.950** (1.775) | **15.000** (0.827) | **0.087** (0.029) | **77.338** |
| 3.5-6 | **1.626** (0.291) | **28.850** (3.464) | **21.917** (2.486) | **15.833** (0.904) | **0.028** (0.011) | **68.254** |
| 6-8.5 | **1.759** (0.271) | **33.042** (3.483) | **26.925** (3.096) | **17.267** (0.998) | **0.028** (0.011) | **79.021** |
| 8.5-11 | **1.006** (0.226) | **38.033** (4.322) | **25.225** (2.160) | **19.558** (1.200) | **0.023** (0.008) | **83.845** |
| 11-13.5 | **0.786** (0.101) | **31.742** (3.895) | **26.300** (0.869) | **21.783** (0.592) | **0.021** (0.011) | **80.632** |
| 13.5-16 | **1.515** (0.035) | **44.817** (2.629) | **31.408** (1.721) | **22.508** (1.234) | **0.035** (0.004) | **100.283** |
| 16-18.5 | **1.608** (0.037) | **57.975** (4.428) | **35.592** (2.295) | **23.892** (1.423) | **0.028** (0.009) | **119.095** |
| 18.5-21 | **1.406** (0.068) | **42.725** (2.792) | **38.392** (4.418) | **26.375** (1.225) | **0.028** (0.010) | **108.926** |
| 21-23.5 | **1.562** (0.080) | **56.842** (0.743) | **48.642** (1.289) | **27.400** (1.760) | **0.043** (0.005) | **134.489** |
| 23.5-26 | **1.395** (0.013) | **54.958** (3.207) | **49.750** (3.299) | **27.433** (1.887) | **0.057** (0.003) | **133.593** |
| 26-28.5 | **1.192** (0.072) | **50.833** (0.313) | **48.217** (2.496) | **25.392** (1.742) | **0.048** (0.007) | **125.682** |
| 28.5-31 | **0.895** (0.050) | **47.075** (2.709) | **41.317** (1.036) | **24.492** (1.229) | **0.036** (0.003) | **113.815** |
| 31-33.5 | **0.689** (0.026) | **40.158** (2.839) | **41.475** (1.609) | **20.300** (0.958) | **0.035** (0.004) | **102.657** |
| 33.5-36 | **0.476** (0.027) | **33.308** (2.267) | **32.808** (1.125) | **16.300** (1.436) | **0.048** (0.012) | **82.940** |
| 36-38.5 | **0.330** (0.007) | **24.592** (0.350) | **24.567** (1.254) | **12.508** (0.989) | **0.028** (0.002) | **62.025** |
| 38.5-41 | **0.205** (0.009) | **16.650** (0.442) | **18.217** (0.797) | **8.692** (0.639) | **0.033** (0.004) | **43.797** |
| 41-43.5 | **0.119** (0.008) | **11.625** (0.288) | **11.592** (1.046) | **8.139** (0.528) | **0.022** (0.002) | **31.497** |
| 43.5-46 | **0.074** (0.005) | **7.288** (0.431) | **8.109** (0.297) | **6.398** (0.502) | **0.008** (0.001) | **21.877** |
| 46-48.5 | **0.047** (0.004) | **4.658** (0.158) | **5.443** (0.309) | **4.892** (0.190) | **0.008** (0.002) | **15.048** |
| 48.5-51 | **0.033** (0.005) | **2.616** (0.054) | **3.314** (0.284) | **3.068** (0.226) | **<0.0005** | **9.031** |
| 51-53.5 | **0.015** (0.004) | **1.270** (0.009) | **1.655** (0.087) | **1.907** (0.103) | **<0.0005** | **4.847** |
| 53.5-56 | **0.011** (0.004) | **0.503** (0.021) | **0.821** (0.044) | **1.697** (0.083) | **<0.0005** | **3.032** |
| 56-58.5 | **0.004** (0.003) | **0.163** (0.014) | **0.241** (0.012) | **1.152** (0.085) | **<0.0005** | **1.560** |
| 58.5-61 | **0.004** (0.003) | **0.059** (0.001) | **0.112** (0.008) | **0.955** (0.074) | **<0.0005** | **1.130** |

## Appendix C 2b (cont.)

Data collected from the sum of two different chemical extractants ($H_2O$ and $NH_4NO_3$): mean values in bold are EXCH concentrations in the Hallen soil. n=3 (replicates).

| Soil depth (cm) | Concentrations (meq/100g) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Al^{3+}$ | $Mn^{2+}$ | $Fe^{2+}$ | Acidity |
| L | **0.378** | **0.152** | **0.390** | **0.662** | **0.035** | **0.013** | **0.003** | **2.506** |
| F | **0.435** | **0.167** | **0.305** | **0.343** | **0.043** | **0.014** | **0.009** | **1.991** |
| H | **0.394** | **0.141** | **0.243** | **0.302** | **0.045** | **0.015** | **0.011** | **2.084** |
| 0-1 | **0.223** | **0.104** | **0.093** | **0.272** | **0.038** | **0.042** | **0.003** | **2.233** |
| 1-3.5 | **0.256** | **0.122** | **0.086** | **0.317** | **0.041** | **0.057** | **0.003** | **2.037** |
| 3.5-6 | **0.197** | **0.105** | **0.090** | **0.296** | **0.042** | **0.052** | **0.004** | **1.901** |
| 6-8.5 | **0.221** | **0.113** | **0.084** | **0.297** | **0.042** | **0.040** | **0.003** | **1.618** |
| 8.5-11 | **0.236** | **0.118** | **0.076** | **0.312** | **0.047** | **0.040** | **0.002** | **1.409** |
| 11-13.5 | **0.191** | **0.093** | **0.087** | **0.251** | **0.042** | **0.031** | **0.001** | **1.315** |
| 13.5-16 | **0.252** | **0.131** | **0.064** | **0.342** | **0.047** | **0.040** | **0.002** | **1.285** |
| 16-18.5 | **0.313** | **0.162** | **0.066** | **0.371** | **0.047** | **0.047** | **0.001** | **1.172** |
| 18.5-21 | **0.261** | **0.155** | **0.065** | **0.340** | **0.040** | **0.042** | **0.001** | **1.119** |
| 21-23.5 | **0.360** | **0.192** | **0.075** | **0.369** | **0.041** | **0.052** | **0.001** | **1.045** |
| 23.5-26 | **0.389** | **0.210** | **0.080** | **0.357** | **0.035** | **0.046** | **0.001** | **0.953** |
| 26-28.5 | **0.423** | **0.234** | **0.090** | **0.349** | **0.027** | **0.042** | **0.001** | **0.910** |
| 28.5-31 | **0.482** | **0.275** | **0.103** | **0.362** | **0.024** | **0.038** | **0.001** | **0.849** |
| 31-33.5 | **0.497** | **0.292** | **0.108** | **0.337** | **0.018** | **0.036** | **<0.001** | **0.811** |
| 33.5-36 | **0.552** | **0.338** | **0.119** | **0.340** | **0.014** | **0.031** | **<0.001** | **0.792** |
| 36-38.5 | **0.557** | **0.351** | **0.117** | **0.315** | **0.010** | **0.032** | **<0.001** | **0.644** |
| 38.5-41 | **0.558** | **0.363** | **0.129** | **0.297** | **0.007** | **0.034** | **<0.001** | **0.587** |
| 41-43.5 | **0.585** | **0.394** | **0.131** | **0.278** | **0.005** | **0.024** | **<0.001** | **0.500** |
| 43.5-46 | **0.588** | **0.405** | **0.131** | **0.249** | **0.004** | **0.021** | **<0.001** | **0.456** |
| 46-48.5 | **0.584** | **0.408** | **0.131** | **0.218** | **0.002** | **0.018** | **<0.001** | **0.354** |
| 48.5-51 | **0.583** | **0.408** | **0.131** | **0.187** | **0.001** | **0.015** | **<0.001** | **0.269** |
| 51-53.5 | **0.616** | **0.435** | **0.137** | **0.172** | **0.001** | **0.013** | **<0.001** | **0.158** |
| 53.5-56 | **0.612** | **0.430** | **0.142** | **0.152** | **<0.001** | **0.010** | **<0.001** | **0.072** |
| 56-58.5 | **0.689** | **0.475** | **0.159** | **0.140** | **<0.001** | **0.006** | **<0.001** | **0.022** |
| 58.5-61 | **0.656** | **0.474** | **0.154** | **0.124** | **<0.001** | **0.003** | **<0.001** | **0.008** |

## Appendix C 3

### pH adjustments: soil/peat sludges

Data collected from 1: 40 soil: water slurries with the pH adjusted using three different acid treatments ($HNO_3$, $H_2SO_4$, HCl). Mean values for soluble metals are shown in bold; data in parentheses are ± standard errors. n=3 (replicates).

Zinc concentration (mg/l)

| Slurry pH | Nitric acid | Hydrochloric acid | Sulphuric acid |
|---|---|---|---|
| pH 3.0 | **0.893** (0.077) | **0.939** (0.032) | **0.976** (0.046) |
| pH 3.5 | **0.739** (0.010) | **0.761** (0.011) | **0.833** (0.021) |
| pH 4.0 | **0.630** (0.011) | **0.643** (0.041) | **0.660** (0.054) |
| pH 4.5 | **0.446** (0.035) | **0.462** (0.028) | **0.613** (0.037) |
| pH 5.0 | **0.303** (0.046) | **0.333** (0.057) | **0.333** (0.076) |
| pH 5.5 | **0.123** (0.011) | **0.123** (0.015) | **0.117** (0.014) |
| pH 6.0 | **0.119** (0.016) | **0.095** (0.025) | **0.072** (0.002) |
| pH 6.5 | **0.048** (0.006) | **0.038** (0.004) | **0.043** (0.004) |
| pH 7.0 | **0.052** (0.006) | **0.051** (0.005) | **0.043** (0.004) |
| pH 7.5 | **0.049** (0.002) | **0.048** (0.003) | **0.049** (0.001) |
| pH 8.0 | **0.032** (0.002) | **0.034** (0.001) | **0.035** (0.002) |
| pH 8.5 | **0.035** (0.001) | **0.036** (0.002) | **0.038** (0.003) |

Lead concentration (mg/l)

| Slurry pH | Nitric acid | Hydrochloric acid | Sulphuric acid |
|---|---|---|---|
| pH 3.0 | **0.092** (0.002) | **0.075** (0.010) | **0.018** (0.001) |
| pH 3.5 | **0.035** (0.007) | **0.034** (0.002) | **0.011** (0.001) |
| pH 4.0 | **0.020** (0.006) | **0.017** (0.004) | **0.006** <0.0005 |
| pH 4.5 | **0.008** (0.001) | **0.008** (0.003) | **0.003** (0.001) |
| pH 5.0 | **0.002** <0.0005 | **0.001** <0.0005 | **0.002** (0.001) |
| pH 5.5 | **0.003** (0.001) | **0.001** <0.0005 | **0.002** (0.001) |
| pH 6.0 | **0.003** (0.001) | **0.003** (0.001) | **0.002** <0.0005 |
| pH 6.5 | **0.002** (0.001) | **0.001** <0.0005 | **0.001** <0.0005 |
| pH 7.0 | **0.004** (0.002) | **0.002** <0.0005 | **0.002** (0.001) |
| pH 7.5 | **0.002** (0.001) | **0.005** (0.001) | **0.003** (0.001) |
| pH 8.0 | **0.003** <0.0005 | **0.002** (0.001) | **0.001** <0.0005 |
| pH 8.5 | **0.004** (0.001) | **0.003** (0.001) | **0.002** (0.001) |

**Appendix C 3 (cont.)**

Cadmium concentration (mg/l)

| Slurry pH | Nitric acid | Hydrochloric acid | Sulphuric acid |
|---|---|---|---|
| pH 3.0 | **0.902** (0.028) | **0.967** (0.010) | **0.926** (0.021) |
| pH 3.5 | **0.863** (0.021) | **0.941** (0.015) | **0.900** (0.009) |
| pH 4.0 | **0.790** (0.016) | **0.919** (0.014) | **0.834** (0.014) |
| pH 4.5 | **0.663** (0.033) | **0.795** (0.016) | **0.704** (0.026) |
| pH 5.0 | **0.410** (0.032) | **0.541** (0.032) | **0.453** (0.035) |
| pH 5.5 | **0.162** (0.008) | **0.206** (0.016) | **0.184** (0.020) |
| pH 6.0 | **0.075** (0.012) | **0.088** (0.001) | **0.085** (0.003) |
| pH 6.5 | **0.026** (0.001) | **0.030** (0.002) | **0.032** (0.002) |
| pH 7.0 | **0.014** (0.001) | **0.014** <0.0005 | **0.013** <0.0005 |
| pH 7.5 | **0.009** <0.0005 | **0.008** <0.0005 | **0.009** (0.001) |
| pH 8.0 | **0.006** <0.0005 | **0.006** <0.0005 | **0.006** <0.0005 |
| pH 8.5 | **0.004** <0.0005 | **0.004** <0.0005 | **0.006** (0.001) |

Copper concentration (mg/l)

| Slurry pH | Nitric acid | Hydrochloric acid | Sulphuric acid |
|---|---|---|---|
| pH 3.0 | **0.071** (0.005) | **0.246** (0.006) | **0.107** (0.010) |
| pH 3.5 | **0.034** (0.003) | **0.135** (0.009) | **0.073** (0.013) |
| pH 4.0 | **0.014** (0.003) | **0.064** (0.016) | **0.025** (0.005) |
| pH 4.5 | **0.010** (0.001) | **0.016** (0.003) | **0.010** (0.004) |
| pH 5.0 | **0.007** <0.0005 | **0.009** (0.003) | **0.006** (0.002) |
| pH 5.5 | **0.007** (0.004) | **0.006** (0.005) | **0.004** (0.002) |
| pH 6.0 | **0.003** (0.002) | **0.003** <0.0005 | **0.003** (0.001) |
| pH 6.5 | **0.003** (0.001) | **0.003** <0.0005 | **0.003** <0.0005 |
| pH 7.0 | **0.002** (0.001) | **0.003** <0.0005 | **0.003** <0.0005 |
| pH 7.5 | **0.002** (0.001) | **0.003** <0.0005 | **0.002** <0.0005 |
| pH 8.0 | **0.004** (0.001) | **0.004** (0.001) | **0.003** <0.0005 |
| pH 8.5 | **0.006** (0.002) | **0.003** <0.0005 | **0.005** (0.002) |

## Appendix C 4

Data collected from 1: 20 soil: water and 1:40 peat: water slurries with the pH adjusted using $HNO_3$. Mean values for soluble metals are presented. n=2 (replicates).

Soil: water slurry metal concentrations (mg/l)

| Slurry pH | Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| pH 3.0 | 1.607 | 0.123 | 0.190 | 1.250 |
| pH 3.5 | 1.587 | 0.075 | 0.110 | 1.139 |
| pH 4.0 | 1.457 | 0.044 | 0.037 | 0.986 |
| pH 4.5 | 1.141 | 0.009 | 0.007 | 0.577 |
| pH 5.0 | 0.509 | 0.005 | 0.002 | 0.220 |
| pH 5.5 | 0.211 | 0.005 | 0.001 | 0.124 |
| pH 6.0 | 0.090 | 0.001 | 0.001 | 0.098 |
| pH 6.5 | 0.044 | 0.002 | 0.002 | 0.086 |
| pH 7.0 | 0.021 | 0.001 | 0,001 | 0.062 |
| pH 7.5 | 0.014 | 0.004 | 0.002 | 0.047 |
| pH 8.0 | 0.012 | 0.006 | 0.002 | 0.048 |
| pH 8.5 | 0.010 | 0.005 | 0.003 | 0.040 |

Peat: water slurry metal concentrations (mg/l)

| Slurry pH | Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| pH 3.0 | 1.442 | 0.015 | 0.150 | 1.945 |
| pH 3.5 | 1.049 | 0.010 | 0.046 | 1.471 |
| pH 4.0 | 0.772 | 0.008 | 0.021 | 1.118 |
| pH 4.5 | 0.540 | 0.014 | 0.011 | 0.800 |
| pH 5.0 | 0.323 | 0.008 | 0.005 | 0.468 |
| pH 5.5 | 0.156 | 0.007 | 0.004 | 0.304 |
| pH 6.0 | 0.070 | 0.011 | 0.003 | 0.125 |
| pH 6.5 | 0.026 | 0.007 | 0.002 | 0.061 |
| pH 7.0 | 0.012 | 0.003 | 0.002 | 0.058 |
| pH 7.5 | 0.008 | 0.004 | 0.003 | 0.051 |

## Appendix C 5

### Hallen 0.1M $NH_4NO_3$ extracts: Heavy metal speciation

Data collected from soil/ammonium nitrate extracts: mean values for exchangeable metals and the various metal species are shown in bold; data in parentheses are ± standard errors. n=3 (replicates).

| Soil depth (cm) | Total soluble (mg/kg) | Cationic (mg/kg) | Anionic (mg/kg) | Neutral (mg/kg) | Low polar (mg/kg) |
|---|---|---|---|---|---|
| | | Cadmium species | | | |
| L/F/H | **0.411** (0.020) | **0.364** (0.014) | **0.003** (0.002) | **0.004** (0.002) | **0.009** (0.004) |
| 0-1 | **1.012** (0.012) | **0.902** (0.010) | **0.002** (0.002) | **0.004** (0.002) | **0.002** (0.000) |
| 8.5-11 | **1.344** (0.004) | **1.222** (0.012) | **0.000** (0.001) | **0.001** (0.001) | **0.005** (0.003) |
| 18.5-21 | **1.432** (0.091) | **1.306** (0.076) | **0.001** (0.000) | **0.004** (0.002) | **0.003** (0.002) |
| 28.5-31 | **1.293** (0.069) | **1.185** (0.061) | **0.001** (0.001) | **0.002** (0.000) | **0.001** (0.000) |
| | | Copper species | | | |
| L/F/H | **0.224** (0.006) | **0.100** (0.009) | **0.044** (0.003) | **0.003** (0.001) | **0.060** (0.006) |
| 0-1 | **0.138** (0.011) | **0.084** (0.009) | **0.007** (0.002) | **0.002** (0.001) | **0.022** (0.006) |
| 8.5-11 | **0.168** (0.008) | **0.122** (0.010) | **0.011** (0.003) | **<0.001** | **0.011** (0.000) |
| 18.5-21 | **0.153** (0.008) | **0.114** (0.008) | **0.006** (0.001) | **0.001** (0.000) | **0.009** (0.001) |
| 28.5-31 | **0.144** (0.005) | **0.089** (0.008) | **0.006** (0.002) | **0.001** (0.001) | **0.015** (0.001) |
| | | Lead species | | | |
| L/F/H | **2.819** (0.135) | **1.480** (0.022) | **0.037** (0.007) | **0.009** (0.001) | **0.130** (0.004) |
| 0-1 | **4.558** (0.128) | **3.977** (0.111) | **0.020** (0.010) | **0.012** (0.003) | **0.025** (0.007) |
| 8.5-11 | **0.161** (0.003) | **0.130** (0.008) | **<0.001** | **0.004** (0.004) | **0.006** (0.006) |
| 18.5-21 | **0.057** (0.001) | **0.034** (0.003) | **0.001** (0.000) | **0.003** (0.003) | **0.010** (0.006) |
| 28.5-31 | **0.048** (0.002) | **0.028** (0.001) | **0.001** (0.000) | **0.001** (0.000) | **0.012** (0.004) |
| | | Zinc species | | | |
| L/F/H | **7.727** (1.340) | **6.098** (0.784) | **0.089** (0.087) | **0.225** (0.045) | **0.530** (0.081) |
| 0-1 | **6.652** (0.149) | **4.248** (0.051) | **0.474** (0.095) | **0.675** (0.054) | **0.432** (0.018) |
| 8.5-11 | **4.206** (0.292) | **2.569** (0.226) | **0.326** (0.006) | **0.498** (0.017) | **0.266** (0.023) |
| 18.5-21 | **2.728** (0.163) | **1.592** (0.114) | **0.215** (0.039) | **0.363** (0.013) | **0.189** (0.006) |
| 28.5-31 | **1.273** (0.094) | **0.726** (0.058) | **0.142** (0.026) | **0.179** (0.007) | **0.132** (0.028) |

## Appendix C 6

### Haw and Hallen water extracts: Heavy metal speciation

Data collected fom soil/water extracts: mean values for soluble metals and the various metal species are shown in bold; data in parentheses are standard errors. n=3 (replicates).

| Soil depth (cm) | Total soluble (mg/kg) | Cationic (mg/kg) | Anionic (mg/kg) | Neutral (mg/kg) | Low polar (mg/kg) |
|---|---|---|---|---|---|
| | | Haw cadmium species | | | |
| L/F/H | **0.0917** (0.0116) | **0.0587** (0.0031) | **0.0019** (0.0013) | **0.0058** (0.0003) | **0.0115** (0.0018) |
| 0-1 | **0.0630** (0.0025) | **0.0346** (0.0008) | **0.0033** (0.0006) | **0.0119** (0.0009) | **0.0060** (0.0008) |
| 1-3.5 | **0.0381** (0.0028) | **0.0226** (0.0020) | **0.0035** (0.0006) | **0.0079** (0.0003) | **0.0036** (0.0004) |
| 3.5-6 | **0.0232** (0.0006) | **0.0107** (0.0007) | **0.0014** (0.0003) | **0.0056** (0.0003) | **0.0045** (0.0002) |
| 6-8.5 | **0.0140** (0.0008) | **0.0060** (0.0004) | **0.0019** (0.0003) | **0.0032** (0.0009) | **0.0027** (0.0007) |
| 8.5-11 | **0.0078** (0.0005) | **0.0038** (0.0003) | **0.0004** (0.0002) | **0.0016** (0.0001) | **0.0016** (0.0004) |
| | | Hallen cadmium species | | | |
| L | **0.0599** (0.0018) | **0.0468** (0.0033) | **0.0011** (0.0003) | **0.0022** (0.0004) | **0.0049** (0.0005) |
| F | **0.0648** (0.0006) | **0.0422** (0.0042) | **0.0013** (0.0008) | **0.0052** (0.0001) | **0.0083** (0.0008) |
| H | **0.0701** (0.0024) | **0.0547** (0.0021) | **0.0005** (0.0003) | **0.0014** (0.0002) | **0.0041** (0.0006) |
| 0-1 | **0.0305** (0.0007) | **0.0221** (0.0004) | **0.0014** (0.0019) | **0.0015** (0.0007) | **0.0039** (0.0002) |
| 1-3.5 | **0.0313** (0.0006) | **0.0278** (0.0014) | **0.0005** (0.0005) | **0.0015** (0.0001) | **0.0031** (0.0004) |
| 3.5-6 | **0.0587** (0.0046) | **0.0470** (0.0007) | **0.0010** (0.0004) | **0.0017** (0.0003) | **0.0037** (0.0002) |
| 6-8.5 | **0.0454** (0.0035) | **0.0383** (0.0029) | **<0.0001** | **0.0030** (0.0007) | **0.0039** (0.0006) |
| 8.5-11 | **0.0387** (0.0022) | **0.0303** (0.0012) | **0.0008** (0.0002) | **0.0026** (0.0001) | **0.0033** (0.0005) |
| 11-13.5 | **0.0431** (0.0047) | **0.0381** (0.0024) | **<0.0001** | **0.0026** (0.0012) | **0.0014** (0.0001) |
| 13.5-16 | **0.0273** (0.0015) | **0.0207** (0.0005) | **0.0006** (0.0007) | **0.0047** (0.0005) | **0.0022** (0.0005) |
| 16-18.5 | **0.0258** (0.0037) | **0.0176** (0.0039) | **0.0015** (0.0004) | **0.0034** (0.0004) | **0.0012** (0.0003) |
| 18.5-21 | **0.0345** (0.0030) | **0.0296** (0.0022) | **0.0015** (0.0007) | **0.0025** (0.0002) | **0.0017** (0.0006) |
| 21-23.5 | **0.0415** (0.0021) | **0.0336** (0.0020) | **0.0018** (0.0001) | **0.0039** (0.0009) | **0.0018** (0.0001) |
| 23.5-26 | **0.0407** (0.0023) | **0.0397** (0.0012) | **<0.0001** | **0.0027** (0.0004) | **0.0016** (0.0002) |
| 26-28.5 | **0.0338** (0.0022) | **0.0271** (0.0029) | **0.0009** (0.0004) | **0.0032** (0.0003) | **0.0016** (0.0005) |
| 28.5-31 | **0.0227** (0.0011) | **0.0196** (0.0010) | **0.0006** (0.0005) | **0.0013** (0.0002) | **0.0017** (0.0004) |
| 31-33.5 | **0.0257** (0.0009) | **0.0211** (0.0009) | **<0.0001** | **0.0014** (0.0004) | **0.0020** (0.0006) |
| 33.5-36 | **0.0195** (0.0012) | **0.0162** (0.0006) | **0.0006** (0.0012) | **0.0031** (0.0007) | **0.0005** (0.0001) |
| 36-38.5 | **0.0181** (0.0015) | **0.0146** (0.0015) | **0.0004** (0.0008) | **0.0033** (0.0011) | **0.0015** (0.0001) |
| 38.5-41 | **0.0174** (0.0004) | **0.0132** (0.0008) | **<0.0001** | **0.0047** (0.0001) | **0.0005** (0.0001) |
| 41-43.5 | **0.0158** (0.0008) | **0.0118** (0.0006) | **0.0009** (0.0002) | **0.0034** (0.0001) | **0.0009** (0.0001) |
| 43.5-46 | **0.0096** (0.0002) | **0.0099** (0.0001) | **0.0007** (0.0002) | **0.0007** (0.0001) | **0.0002** (0.0001) |
| 46-48.5 | **0.0083** (0.0005) | **0.0076** (0.0005) | **0.0002** (0.0001) | **0.0007** (0.0001) | **0.0004** (0.0001) |
| 48.5-51 | **0.0066** (0.0005) | **0.0048** (0.0001) | **0.0004** (0.0004) | **0.0009** (0.0005) | **0.0001** (0.0001) |

**Appendix C 6 (cont.)**

| Soil depth (cm) | Total soluble (mg/kg) | Cationic (mg/kg) | Anionic (mg/kg) | Neutral (mg/kg) | Low polar (mg/kg) |
|---|---|---|---|---|---|
| | | | Haw copper species | | |
| L/F/H | **0.1382** (0.0284) | **0.0021** (0.0014) | **0.0706** (0.0147) | **0.0027** (0.0010) | **0.0468** (0.0121) |
| 0-1 | **0.1303** (0.0135) | **0.0025** (0.0022) | **0.0858** (0.0079) | **0.0054** (0.0008) | **0.0321** (0.0033) |
| 1-3.5 | **0.0866** (0.0136) | **0.0014** (0.0008) | **0.0587** (0.0123) | **0.0037** (0.0008) | **0.0203** (0.0036) |
| 3.5-6 | **0.0872** (0.0084) | **<0.0001** | **0.0584** (0.0129) | **0.0074** (0.0016) | **0.0178** (0.0012) |
| 6-8.5 | **0.0807** (0.0159) | **<0.0001** | **0.0507** (0.0144) | **0.0072** (0.0026) | **0.0156** (0.0030) |
| 8.5-11 | **0.0574** (0.0119) | **<0.0001** | **0.0296** (0.0109) | **0.0073** (0.0040) | **0.0138** (0.0031) |
| | | | Hallen copper species | | |
| L | **0.3351** (0.0046) | **0.0070** (0.0041) | **0.1560** (0.0011) | **0.0270** (0.0007) | **0.1122** (0.0032) |
| F | **0.2616** (0.0078) | **0.0397** (0.0078) | **0.1014** (0.0014) | **0.0128** (0.0009) | **0.0885** (0.0047) |
| H | **0.1330** (0.0037) | **0.0130** (0.0031) | **0.0430** (0.0022) | **0.0060** (0.0005) | **0.0530** (0.0025) |
| 0-1 | **0.1475** (0.0040) | **0.0285** (0.0054) | **0.0547** (0.0060) | **0.0129** (0.0022) | **0.0485** (0.0012) |
| 1-3.5 | **0.1563** (0.0021) | **0.0320** (0.0010) | **0.0670** (0.0010) | **0.0153** (0.0004) | **0.0537** (0.0047) |
| 3.5-6 | **0.1472** (0.0038) | **0.0146** (0.0082) | **0.0487** (0.0029) | **0.0280** (0.0039) | **0.0611** (0.0077) |
| 6-8.5 | **0.0958** (0.0023) | **0.0139** (0.0018) | **0.0339** (0.0026) | **0.0050** (0.0015) | **0.0357** (0.0044) |
| 8.5-11 | **0.1149** (0.0068) | **0.0184** (0.0068) | **0.0416** (0.0038) | **0.0096** (0.0011) | **0.0287** (0.0070) |
| 11-13.5 | **0.0804** (0.0028) | **0.0068** (0.0017) | **0.0351** (0.0014) | **0.0060** (0.0008) | **0.0306** (0.0011) |
| 13.5-16 | **0.0539** (0.0074) | **0.0091** (0.0018) | **0.0182** (0.0036) | **0.0059** (0.0001) | **0.0226** (0.0027) |
| 16-18.5 | **0.0492** (0.0020) | **0.0073** (0.0018) | **0.0175** (0.0021) | **0.0038** (0.0011) | **0.0220** (0.0037) |
| 18.5-21 | **0.0482** (0.0036) | **0.0074** (0.0005) | **0.0151** (0.0012) | **0.0055** (0.0011) | **0.0153** (0.0043) |
| 21-23.5 | **0.0376** (0.0042) | **0.0020** (0.0001) | **0.0093** (0.0003) | **0.0076** (0.0016) | **0.0194** (0.0017) |
| 23.5-26 | **0.0658** (0.0015) | **0.0064** (0.0009) | **0.0066** (0.0007) | **0.0285** (0.0019) | **0.0321** (0.0008) |
| 26-28.5 | **0.0715** (0.0013) | **0.0013** (0.0002) | **0.0060** (0.0010) | **0.0290** (0.0017) | **0.0338** (0.0021) |
| 28.5-31 | **0.0539** (0.0078) | **0.0143** (0.0054) | **0.0105** (0.0026) | **0.0063** (0.0014) | **0.0151** (0.0027) |
| 31-33.5 | **0.0299** (0.0029) | **0.0058** (0.0008) | **0.0096** (0.0019) | **0.0034** (0.0008) | **0.0106** (0.0009) |
| 33.5-36 | **0.0293** (0.0007) | **0.0064** (0.0016) | **0.0075** (0.0019) | **0.0021** (0.0003) | **0.0085** (0.0006) |
| 36-38.5 | **0.0269** (0.0014) | **0.0055** (0.0001) | **0.0064** (0.0011) | **0.0038** (0.0010) | **0.0088** (0.0007) |
| 38.5-41 | **0.0231** (0.0010) | **0.0042** (0.0003) | **0.0067** (0.0004) | **0.0013** (0.0004) | **0.0108** (0.0032) |
| 41-43.5 | **0.0240** (0.0003) | **0.0041** (0.0007) | **0.0050** (0.0006) | **0.0031** (0.0004) | **0.0089** (0.0016) |
| 43.5-46 | **0.0335** (0.0043) | **0.0048** (0.0019) | **0.0040** (0.0002) | **0.0116** (0.0005) | **0.0140** (0.0006) |
| 46-48.5 | **0.0432** (0.0025) | **0.0086** (0.0029) | **0.0080** (0.0037) | **0.0102** (0.0022) | **0.0142** (0.0018) |
| 48.5-51 | **0.0424** (0.0029) | **0.0152** (0.0010) | **0.0051** (0.0009) | **0.0062** (0.0011) | **0.0113** (0.0026) |

**Appendix C 6 (cont.)**

| Soil depth (cm) | Total soluble (mg/kg) | Cationic (mg/kg) | Anionic (mg/kg) | Neutral (mg/kg) | Low polar (mg/kg) |
|---|---|---|---|---|---|
| | | | Haw lead species | | |
| L/F/H | **0.1978** (0.0449) | **0.0971** (0.0010) | **0.0473** (0.0047) | **0.0246** (0.0028) | **0.0673** (0.0091) |
| 0-1 | **0.0495** (0.0020) | **0.0007** (0.0026) | **0.0206** (0.0020) | **0.0181** (0.0021) | **0.0109** (0.0008) |
| 1-3.5 | **0.0207** (0.0014) | **0.0025** (0.0036) | **0.0060** (0.0036) | **0.0093** (0.0033) | **0.0084** (0.0019) |
| 3.5-6 | **0.0287** (0.0034) | **0.0004** (0.0023) | **0.0052** (0.0003) | **0.0029** (0.0017) | **0.0146** (0.0049) |
| 6-8.5 | **0.0346** (0.0020) | **0.0009** (0.0039) | **0.0044** (0.0031) | **0.0140** (0.0009) | **0.0188** (0.0013) |
| 8.5-11 | **0.0316** (0.0004) | **0.0028** (0.0005) | **0.0041** (0.0008) | **0.0086** (0.0004) | **0.0181** (0.0043) |
| | | | Hallen lead species | | |
| L | **1.2600** (0.0220) | **0.6273** (0.0312) | **0.2173** (0.0127) | **0.0227** (0.0021) | **0.1400** (0.0113) |
| F | **1.2122** (0.0402) | **0.6161** (0.0483) | **0.1616** (0.0193) | **0.0177** (0.0026) | **0.2227** (0.0191) |
| H | **1.0811** (0.0298) | **0.5813** (0.0261) | **0.1713** (0.0114) | **0.0187** (0.0017) | **0.1817** (0.0105) |
| 0-1 | **0.1065** (0.0030) | **0.0465** (0.0017) | **0.0123** (0.0003) | **0.0117** (0.0010) | **0.0206** (0.0011) |
| 1-3.5 | **0.0527** (0.0029) | **0.0382** (0.0044) | **0.0018** (0.0004) | **0.0127** (0.0011) | **0.0134** (0.0008) |
| 3.5-6 | **0.0324** (0.0009) | **0.0238** (0.0034) | **0.0034** (0.0007) | **0.0066** (0.0011) | **0.0102** (0.0004) |
| 6-8.5 | **0.0331** (0.0007) | **0.0229** (0.0023) | **0.0052** (0.0009) | **0.0078** (0.0017) | **0.0112** (0.0014) |
| 8.5-11 | **0.0489** (0.0004) | **0.0211** (0.0006) | **0.0040** (0.0008) | **0.0130** (0.0013) | **0.0116** (0.0008) |
| 11-13.5 | **0.0305** (0.0022) | **0.0178** (0.0025) | **0.0058** (0.0013) | **0.0106** (0.0001) | **0.0111** (0.0043) |
| 13.5-16 | **0.0331** (0.0021) | **0.0102** (0.0023) | **0.0108** (0.0023) | **0.0099** (0.0026) | **0.0106** (0.0019) |
| 16-18.5 | **0.0339** (0.0037) | **0.0119** (0.0007) | **0.0084** (0.0009) | **0.0115** (0.0006) | **0.0093** (0.0014) |
| 18.5-21 | **0.0259** (0.0007) | **0.0109** (0.0003) | **0.0075** (0.0006) | **0.0055** (0.0002) | **0.0079** (0.0005) |
| 21-23.5 | **0.0323** (0.0020) | **0.0113** (0.0027) | **0.0031** (0.0040) | **0.0110** (0.0015) | **0.0075** (0.0011) |
| 23.5-26 | **0.0315** (0.0019) | **0.0201** (0.0035) | **0.0012** (0.0002) | **0.0081** (0.0008) | **0.0121** (0.0007) |
| 26-28.5 | **0.0367** (0.0008) | **0.0160** (0.0010) | **0.0049** (0.0028) | **0.0099** (0.0011) | **0.0136** (0.0005) |
| 28.5-31 | **0.0142** (0.0004) | **0.0044** (0.0008) | **0.0030** (0.0009) | **0.0027** (0.0001) | **0.0043** (0.0007) |
| 31-33.5 | **0.0251** (0.0017) | **0.0110** (0.0009) | **0.0035** (0.0008) | **0.0041** (0.0009) | **0.0092** (0.0007) |
| 33.5-36 | **0.0234** (0.0015) | **0.0091** (0.0013) | **0.0013** (0.0003) | **0.0045** (0.0005) | **0.0076** (0.0010) |
| 36-38.5 | **0.0147** (0.0009) | **0.0081** (0.0010) | **0.0005** (0.0006) | **0.0059** (0.0009) | **0.0045** (0.0005) |
| 38.5-41 | **0.0179** (0.0029) | **0.0083** (0.0025) | **<0.0001** | **0.0064** (0.0024) | **0.0024** (0.0008) |
| 41-43.5 | **0.0072** (0.0006) | **0.0035** (0.0005) | **<0.0001** | **0.0045** (0.0004) | **0.0018** (0.0004) |
| 43.5-46 | **0.0058** (0.0032) | **0.0040** (0.0003) | **<0.0001** | **0.0020** (0.0001) | **0.0002** (0.0001) |
| 46-48.5 | **0.0037** (0.0007) | **0.0036** (0.0004) | **<0.0001** | **0.0017** (0.0003) | **0.0004** (0.0001) |
| 48.5-51 | **0.0029** (0.0009) | **0.0035** (0.0006) | **<0.0001** | **0.0018** (0.0005) | **0.0004** (0.0001) |

Appendix C 6 (cont.)

| Soil depth (cm) | Total soluble (mg/kg) | Cationic (mg/kg) | Anionic (mg/kg) | Neutral (mg/kg) | Low polar (mg/kg) |
|---|---|---|---|---|---|
| | | Haw zinc species | | | |
| L/F/H | **7.727** (1.340) | **6.098** (0.784) | **0.089** (0.087) | **0.225** (0.045) | **0.530** (0.081) |
| 0-1 | **6.652** (0.149) | **4.248** (0.051) | **0.474** (0.095) | **0.675** (0.054) | **0.432** (0.018) |
| 1-3.5 | **4.206** (0.292) | **2.569** (0.226) | **0.326** (0.006) | **0.498** (0.017) | **0.266** (0.023) |
| 3.5-6 | **2.728** (0.163) | **1.592** (0.114) | **0.215** (0.039) | **0.363** (0.013) | **0.189** (0.006) |
| 6-8.5 | **1.273** (0.094) | **0.726** (0.058) | **0.142** (0.026) | **0.179** (0.007) | **0.132** (0.028) |
| 8.5-11 | **0.661** (0.033) | **0.287** (0.071) | **0.083** (0.018) | **0.107** (0.001) | **0.120** (0.010) |
| | | Hallen zinc species | | | |
| L | **4.598** (0.205) | **3.725** (0.184) | **0.038** (0.008) | **0.176** (0.016) | **0.505** (0.031) |
| F | **4.744** (0.135) | **3.962** (0.126) | **0.024** (0.014) | **0.114** (0.009) | **0.529** (0.029) |
| H | **3.872** (0.167) | **3.226** (0.151) | **0.006** (0.002) | **0.063** (0.006) | **0.272** (0.019) |
| 0-1 | **1.725** (0.210) | **1.324** (0.162) | **0.069** (0.014) | **0.096** (0.004) | **0.205** (0.016) |
| 1-3.5 | **1.665** (0.041) | **1.327** (0.046) | **0.058** (0.004) | **0.058** (0.003) | **0.140** (0.002) |
| 3.5-6 | **2.233** (0.020) | **1.812** (0.046) | **0.011** (0.006) | **0.115** (0.008) | **0.159** (0.008) |
| 6-8.5 | **1.777** (0.106) | **1.435** (0.098) | **0.044** (0.014) | **0.098** (0.012) | **0.143** (0.006) |
| 8.5-11 | **1.953** (0.149) | **1.507** (0.091) | **0.122** (0.020) | **0.119** (0.010) | **0.148** (0.005) |
| 11-13.5 | **2.097** (0.110) | **1.640** (0.070) | **0.109** (0.022) | **0.123** (0.018) | **0.127** (0.006) |
| 13.5-16 | **1.562** (0.081) | **1.029** (0.046) | **0.199** (0.059) | **0.175** (0.022) | **0.103** (0.003) |
| 16-18.5 | **1.366** (0.229) | **0.807** (0.111) | **0.138** (0.028) | **0.174** (0.011) | **0.086** (0.005) |
| 18.5-21 | **1.225** (0.277) | **0.956** (0.168) | **0.094** (0.060) | **0.108** (0.027) | **0.095** (0.023) |
| 21-23.5 | **1.557** (0.155) | **1.104** (0.127) | **0.181** (0.036) | **0.163** (0.021) | **0.089** (0.016) |
| 23.5-26 | **1.924** (0.029) | **1.666** (0.058) | **0.076** (0.008) | **0.121** (0.006) | **0.191** (0.047) |
| 26-28.5 | **1.824** (0.066) | **1.378** (0.062) | **0.110** (0.018) | **0.246** (0.017) | **0.233** (0.014) |
| 28.5-31 | **1.674** (0.061) | **1.309** (0.057) | **0.102** (0.025) | **0.133** (0.010) | **0.172** (0.008) |
| 31-33.5 | **1.632** (0.016) | **1.247** (0.031) | **0.117** (0.060) | **0.081** (0.023) | **0.188** (0.010) |
| 33.5-36 | **1.465** (0.139) | **0.885** (0.121) | **0.153** (0.140) | **0.142** (0.046) | **0.217** (0.017) |
| 36-38.5 | **0.679** (0.035) | **0.454** (0.026) | **0.038** (0.003) | **0.083** (0.025) | **0.051** (0.012) |
| 38.5-41 | **0.519** (0.025) | **0.358** (0.026) | **0.022** (0.003) | **0.070** (0.025) | **0.031** (0.012) |
| 41-43.5 | **0.329** (0.011) | **0.195** (0.008) | **0.020** (0.009) | **0.048** (0.017) | **0.022** (0.005) |
| 43.5-46 | **0.413** (0.035) | **0.347** (0.018) | **0.027** (0.006) | **0.064** (0.002) | **0.020** (0.002) |
| 46-48.5 | **0.482** (0.102) | **0.360** (0.099) | **0.018** (0.040) | **0.078** (0.016) | **0.005** (0.005) |
| 48.5-51 | **0.363** (0.035) | **0.281** (0.023) | **0.032** (0.014) | **0.034** (0.005) | **0.022** (0.012) |

## Appendix C 7a

### Haw cations and anions in soil/water extractions solution (meq/l)

| Soil depth (cm) | $Ca^{2+}$ | $Mg^{2+}$ | $K^{+}$ | $Na^{+}$ | $Fe^{2+}$ | $Al^{3+}$ | $Mn^{2+}$ | $NO_3^{-}$ | $SO_4^{2-}$ | $Cl^{-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| L/F/H | 17.097 | 4.389 | 32.984 | 17.274 | 0.126 | 0.374 | 0.035 | 16.782 | 9.031 | 16.578 |
| 0-1 | 5.645 | 1.007 | 6.426 | 6.783 | 0.332 | 0.278 | 0.022 | 3.629 | 2.846 | 10.920 |
| 1-3.5 | 4.360 | 0.678 | 4.201 | 4.446 | 0.264 | 0.189 | 0.009 | 2.038 | 2.977 | 7.457 |
| 3.5-6 | 5.720 | 0.946 | 5.333 | 5.294 | 0.293 | 0.302 | 0.014 | 1.380 | 3.934 | 9.296 |
| 6-8.5 | 3.449 | 0.550 | 2.347 | 3.413 | 0.205 | 0.156 | 0.006 | 1.103 | 2.792 | 5.669 |
| 8.5-11 | 2.950 | 0.483 | 1.778 | 3.924 | 0.221 | 0.169 | 0.006 | 0.535 | 2.752 | 4.010 |
| 11-13.5 | 2.741 | 0.488 | 1.516 | 3.783 | 0.190 | 0.207 | 0.006 | 0.577 | 2.899 | 2.905 |
| 13.5-16 | 2.944 | 0.452 | 1.675 | 4.131 | 0.184 | 0.244 | 0.007 | 0.432 | 2.886 | 3.052 |
| 16-18.5 | 2.729 | 0.493 | 1.675 | 4.077 | 0.194 | 0.337 | 0.008 | 0.429 | 2.908 | 3.012 |
| 18.5-21 | 2.551 | 0.385 | 1.490 | 3.718 | 0.208 | 0.170 | 0.006 | 0.342 | 3.303 | 2.950 |
| 21-23.5 | 2.065 | 0.457 | 1.765 | 3.392 | 0.226 | 0.095 | 0.007 | 0.361 | 2.729 | 3.187 |
| 23.5-26 | 1.839 | 0.303 | 1.356 | 3.370 | 0.210 | 0.121 | 0.005 | 0.497 | 2.793 | 3.283 |
| 26-28.5 | 1.821 | 0.278 | 1.215 | 3.174 | 0.188 | 0.188 | 0.003 | 0.419 | 2.728 | 3.164 |
| 28.5-31 | 1.768 | 0.267 | 1.362 | 3.076 | 0.237 | 0.123 | 0.005 | 0.294 | 2.806 | 3.029 |
| 31-33.5 | 1.519 | 0.221 | 1.068 | 2.674 | 0.252 | 0.101 | 0.007 | 0.558 | 2.844 | 2.724 |
| 33.5-36 | 1.563 | 0.293 | 1.260 | 2.555 | 0.325 | 0.093 | 0.002 | 0.784 | 2.737 | 2.583 |
| 36-38.5 | 1.606 | 0.190 | 0.927 | 2.903 | 0.485 | 0.117 | 0.003 | 0.858 | 2.736 | 2.504 |
| 38.5-41 | 1.491 | 0.180 | 0.665 | 2.729 | 0.491 | 0.113 | 0.002 | 0.497 | 2.641 | 2.279 |
| 41-46 | 1.775 | 0.231 | 0.742 | 2.653 | 0.494 | 0.095 | 0.003 | 0.596 | 2.620 | 2.304 |

## Appendix C 7b

### Hallen cations and anions in soil/water extractions (meq/l)

| Soil depth (cm) | Ca2+ | Mg2+ | K+ | Na+ | Fe2+ | Al3+ | Mn2+ | $HPO_4^{2-}$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| L | 17.372 | 8.111 | 55.537 | 35.233 | 0.383 | 1.733 | 0.581 | | | | |
| F | 14.174 | 7.137 | 21.319 | 28.765 | 0.824 | 2.023 | 0.480 | 0.804 | 21.402 | 13.908 | 18.231 |
| H | 11.209 | 4.965 | 18.071 | 21.264 | 0.842 | 2.497 | 0.441 | | | | |
| 0-1 | 0.767 | 0.737 | 3.922 | 4.725 | 0.340 | 0.823 | 0.167 | 0.592 | 3.738 | 3.780 | 6.430 |
| 1-3.5 | 1.198 | 0.925 | 5.452 | 6.160 | 0.185 | 0.587 | 0.378 | 0.390 | 1.703 | 3.982 | 6.278 |
| 3.5-6 | 1.840 | 1.275 | 6.834 | 7.175 | 0.225 | 0.570 | 0.554 | 1.381 | 1.271 | 3.810 | 6.684 |
| 6-8.5 | 2.075 | 1.268 | 6.991 | 7.255 | 0.242 | 0.449 | 0.406 | 1.268 | 1.193 | 3.744 | 8.010 |
| 8.5-11 | 1.150 | 0.675 | 4.395 | 5.037 | 0.296 | 0.330 | 0.202 | 0.896 | 1.290 | 3.652 | 6.035 |
| 11-13.5 | 1.237 | 0.565 | 3.986 | 6.914 | 0.115 | 0.223 | 0.153 | 0.324 | 1.674 | 3.745 | 6.131 |
| 13.5-16 | 1.412 | 0.946 | 6.846 | 3.957 | 0.427 | 0.333 | 0.263 | 0.472 | 1.258 | 3.955 | 5.161 |
| 16-18.5 | 1.512 | 0.946 | 7.196 | 4.160 | 0.192 | 0.209 | 0.264 | 0.528 | 1.577 | 4.096 | 5.579 |
| 18.5-21 | 1.553 | 0.856 | 6.672 | 4.059 | 0.165 | 0.157 | 0.230 | 0.490 | 1.793 | 4.387 | 4.281 |
| 21-23.5 | 1.907 | 1.162 | 6.991 | 4.385 | 0.198 | 0.132 | 0.263 | 1.018 | 2.400 | 5.113 | 4.490 |
| 23.5-26 | 1.888 | 1.162 | 6.484 | 4.443 | 0.112 | 0.119 | 0.234 | 1.167 | 2.667 | 5.109 | 4.388 |
| 26-28.5 | 1.909 | 1.192 | 5.759 | 5.015 | 0.119 | 0.090 | 0.201 | 1.123 | 2.548 | 5.048 | 3.706 |
| 28.5-31 | 1.722 | 1.148 | 5.073 | 4.704 | 0.116 | 0.064 | 0.155 | 1.036 | 2.126 | 4.437 | 3.599 |
| 31-33.5 | 1.657 | 1.127 | 4.327 | 4.544 | 0.075 | 0.058 | 0.125 | 0.995 | 1.606 | 4.451 | 2.967 |
| 33.5-36 | 1.474 | 1.069 | 3.504 | 4.095 | 0.028 | 0.038 | 0.087 | 0.806 | 1.313 | 3.788 | 2.911 |
| 36-38.5 | 1.441 | 1.035 | 2.929 | 3.653 | 0.017 | 0.029 | 0.084 | 0.856 | 1.010 | 4.113 | 2.713 |
| 38.5-41 | 1.403 | 1.062 | 2.639 | 3.935 | 0.021 | 0.027 | 0.089 | 0.674 | 1.139 | 4.179 | 2.499 |
| 41-43.5 | 1.250 | 1.011 | 2.200 | 3.660 | 0.016 | 0.022 | 0.056 | 0.701 | 0.793 | 2.764 | 2.775 |
| 43.5-46 | 1.389 | 1.097 | 1.982 | 3.870 | 0.016 | 0.014 | 0.053 | 0.982 | 0.442 | 2.997 | 3.097 |
| 46-48.5 | 1.320 | 1.052 | 1.484 | 3.392 | 0.010 | 0.011 | 0.043 | 0.753 | 0.784 | 2.940 | 2.854 |
| 48.5-51 | 1.306 | 1.045 | 1.147 | 3.153 | 0.022 | 0.010 | 0.036 | 0.419 | 0.558 | 2.963 | 2.634 |
| 51-53.5 | 1.135 | 0.953 | 0.925 | 2.653 | 0.017 | 0.012 | 0.024 | Nd | 0.706 | 3.981 | 2.166 |
| 53.5-56 | 1.112 | 0.980 | 0.712 | 2.950 | 0.017 | 0.009 | 0.020 | Nd | 0.471 | 2.200 | 2.465 |
| 56-58.5 | 0.925 | 0.757 | 0.388 | 2.087 | 0.011 | 0.010 | 0.009 | Nd | 0.364 | 1.541 | 1.297 |
| 58.5-61 | 0.753 | 0.606 | 0.234 | 1.334 | 0.011 | 0.009 | 0.005 | Nd | 0.326 | 1.128 | 0.513 |

## Appendix 8a

### *Holcus lanatus*: Haw data

Data collected from *Holcus lanatus* grown on Haw 1987 soil: mean values for plant height, weight and tissue metal concentrations are shown in bold; data within parentheses are ± standard errors. n=10 (replicates).

| Soil depth (cm) | Plant height (cm) | Plant weight (mg) | Plant Cd (mg/kg) | Plant Cu (mg/kg) | Plant Pb (mg/kg) | Plant Zn (mg/kg) |
|---|---|---|---|---|---|---|
| 0-1 | **27.3** (0.62) | **276.6** (11.1) | **8.22** (1.84) | **5.92** (0.49) | **0.58** (0.04) | **112.0** (6.8) |
| 1-3.5 | **25.2** (1.06) | **224.4** (11.1) | **9.76** (1.96) | **6.77** (0.61) | **0.38** (0.07) | **99.2** (7.9) |
| 3.5-6 | **22.5** (0.82) | **217.1** (13.7) | **10.18** (1.27) | **7.97** (0.89) | **0.22** (0.02) | **124.5** (12.5) |
| 6-8.5 | **24.5** (0.94) | **215.3** (11.2) | **6.57** (1.05) | **6.50** (0.57) | **0.29** (0.04) | **76.7** (6.2) |
| 8.5-11 | **19.9** (0.69) | **150.8** ( 9.4) | **2.80** (0.63) | **6.78** (0.64) | **0.45** (0.09) | **63.1** (6.4) |
| 11-13.5 | **21.6** (0.75) | **139.3** ( 6.0) | **2.15** (0.39) | **7.88** (1.14) | **0.22** (0.06) | **41.1** (3.7) |
| 13.5-16 | **18.1** (1.17) | **104.9** (10.0) | **2.21** (0.46) | **8.91** (0.97) | **0.21** (0.09) | **49.1** (4.5) |
| 16-18.5 | **19.3** (1.04) | **94.6** ( 8.0) | **1.27** (0.16) | **9.11** (1.93) | **0.11** (0.05) | **50.2** (4.1) |
| 18.5-21 | **18.0** (0.83) | **78.1** (10.6) | **2.01** (0.44) | **9.56** (1.32) | **0.16** (0.04) | **54.0** (5.0) |
| 21-23.5 | **20.2** (0.64) | **94.3** ( 4.9) | **1.21** (0.22) | **7.11** (1.11) | **0.22** (0.08) | **40.1** (3.0) |
| 23.5-26 | **18.8** (1.21) | **72.2** ( 5.8) | **0.96** (0.26) | **7.55** (0.99) | **0.16** (0.07) | **52.6** (4.7) |
| 26-28.5 | **17.5** (1.06) | **51.6** ( 4.8) | **1.07** (0.21) | **9.27** (1.89) | **0.27** (0.02) | **52.8** (4.0) |
| 28.5-31 | **14.1** (1.55) | **33.3** ( 3.9) | **0.88** (0.16) | **5.00** (1.48) | **0.21** (0.07) | **72.7** (7.3) |
| 31-33.5 | **12.6** (1.12) | **29.4** ( 2.8) | **0.91** (0.32) | **4.97** (1.41) | **0.07** (0.05) | **71.2** (4.7) |
| 33.5-36 | **11.4** (0.96) | **27.1** ( 3.6) | **0.36** (0.14) | **5.13** (0.64) | **<0.1** | **66.1** (4.2) |
| 36-38.5 | **12.2** (1.03) | **39.4** ( 2.2) | **0.54** (0.10) | **3.73** (0.83) | **<0.1** | **38.4** (8.0) |
| 38.5-41 | **8.5** (0.49) | **20.4** ( 2.3) | **0.33** (0.13) | **4.36** (1.18) | **<0.1** | **67.0** (3.6) |
| 41-46 | **15.8** (0.61) | **38.8** ( 1.5) | **0.22** (0.06) | **4.18** (1.30) | **<0.1** | **30.0** (4.5) |

## Appendix 8b

### *Holcus lanatus*: Hallen data

Data collected from *Holcus lanatus* grown on Hallen 1987 soil: mean values for plant height, weight and tissue metal concentrations are shown in bold; data within parentheses are ± standard errors. n=10 (replicates).

| Soil depth (cm) | Plant height (cm) | Plant weight (mg) | Plant Cd (mg/kg) | Plant Cu (mg/kg) | Plant Pb (mg/kg) | Plant Zn (mg/kg) |
|---|---|---|---|---|---|---|
| 0-1 | **22.2** (0.8) | **87.6** (3.4) | **3.10** (0.46) | **7.75** (1.36) | **8.06** (0.46) | **97.8** (6.0) |
| 1-3.5 | **19.5** (0.9) | **53.7** (2.0) | **3.77** (0.71) | **6.15** (0.89) | **3.72** (0.27) | **128.1** (11.2) |
| 3.5-6 | **15.8** (0.9) | **31.0** (2.8) | **3.10** (0.35) | **5.92** (1.26) | **2.27** (0.40) | **102.0** (9.0) |
| 6-8.5 | **14.8** (0.8) | **22.7** (1.7) | **3.60** (0.62) | **4.35** (1.18) | **1.58** (0.22) | **101.5** (13.5) |
| 8.5-11 | **16.9** (1.0) | **30.4** (1.7) | **3.90** (0.48) | **5.60** (0.92) | **1.60** (0.18) | **129.6** (14.9) |
| 11-13.5 | **16.1** (0.5) | **29.0** (1.3) | **6.30** (1.57) | **5.20** (1.52) | **1.92** (0.54) | **134.2** (12.2) |
| 13.5-16 | **16.1** (0.6) | **27.9** (1.7) | **7.07** (1.18) | **7.51** (0.86) | **2.38** (0.63) | **173.6** (19.6) |
| 16-18.5 | **14.3** (0.6) | **24.7** (1.2) | **7.89** (1.55) | **7.93** (1.71) | **1.79** (0.32) | **230.0** (16.2) |
| 18.5-21 | **13.2** (1.0) | **23.7** (1.2) | **9.42** (1.66) | **9.17** (1.98) | **1.41** (0.45) | **221.6** (19.8) |
| 21-23.5 | **10.1** (1.0) | **15.8** (0.9) | **10.08** (2.10) | **7.32** (2.04) | **1.27** (0.19) | **268.3** (22.8) |
| 23.5-26 | **10.2** (1.1) | **15.6** (1.5) | **10.88** (2.98) | **8.59** (2.23) | **0.79** (0.30) | **316.9** (23.0) |
| 26-28.5 | **10.0** (0.7) | **17.3** (1.2) | **14.71** (3.19) | **10.32** (3.25) | **1.03** (0.37) | **289.7** (27.8) |
| 28.5-31 | **9.8** (0.6) | **14.4** (1.1) | **22.07** (5.60) | **13.59** (3.41) | **1.86** (0.59) | **279.0** (33.5) |
| 31-33.5 | **13.5** (1.3) | **20.6** (1.6) | **11.08** (1.64) | **8.38** (2.74) | **1.51** (0.23) | **181.0** (21.8) |
| 33.5-36 | **12.3** (0.9) | **21.0** (1.7) | **9.95** (1.79) | **3.74** (2.04) | **1.18** (0.42) | **182.5** (22.3) |
| 36-38.5 | **11.6** (0.9) | **16.5** (1.3) | **10.62** (1.69) | **6.78** (2.30) | **1.34** (0.41) | **146.2** (14.2) |
| 38.5-41 | **11.0** (1.1) | **16.9** (1.5) | **15.81** (3.10) | **9.41** (2.22) | **1.97** (0.38) | **161.6** (11.9) |
| 41-43.5 | **10.5** (0.6) | **16.2** (1.2) | **19.40** (3.21) | **10.96** (3.26) | **1.59** (0.30) | **149.8** (11.2) |
| 43.5-46 | **11.1** (1.0) | **16.1** (1.8) | **10.07** (3.72) | **9.95** (3.06) | **0.26** (0.11) | **139.4** (15.3) |
| 46-48.5 | **12.7** (1.0) | **21.6** (1.1) | **5.66** (0.91) | **10.15** (2.38) | **0.50** (0.20) | **125.3** (13.3) |
| 48.5-51 | **13.4** (0.6) | **29.3** (0.9) | **3.39** (0.31) | **10.34** (2.79) | **0.40** (0.18) | **64.1** (3.4) |
| 51-53.5 | **15.8** (0.9) | **30.0** (1.4) | **2.65** (0.27) | **10.85** (2.43) | **0.32** (0.20) | **51.7** (5.0) |
| 53.5-56 | **16.2** (1.4) | **23.5** (2.4) | **1.67** (0.34) | **15.05** (2.79) | **0.35** (0.36) | **51.5** (2.6) |
| 56-58.5 | **18.0** (1.0) | **29.7** (1.3) | **1.14** (0.14) | **13.90** (2.58) | **0.47** (0.11) | **44.5** (2.9) |
| 58.5-61 | **20.2** (0.9) | **39.2** (1.7) | **0.55** (0.11) | **12.99** (2.81) | **0.40** (0.17) | **40.2** (2.1) |

## Appendix 9

### Sunflower Experiment: Mendip loam

Data collected from *Helianthus annuus* grown on Mendip loam: mean values for plant height, weight and tissue metal concentrations are shown in bold; data in parentheses are ± standard errors. n=10 (replicates).

| Metal/pH treatments | Plant height (cm) | Plant weight (grams) | Plant Cd (mg/kg) | Plant Cu (mg/kg) | Plant Pb (mg/kg) | Plant Zn (mg/kg) |
|---|---|---|---|---|---|---|
| Control | | | | | | |
| pH 3.75 | **39.2** (2.3) | **1.7** (0.2) | **20.4** (1.7) | **27.3** (1.2) | **10.2** (0.7) | **482.8** (23.9) |
| pH 4.75 | **43.3** (0.9) | **2.6** (0.1) | **9.6** (1.3) | **20.9** (1.5) | **7.1** (0.5) | **275.0** (22.1) |
| pH 5.25 | **42.2** (1.3) | **2.3** (0.2) | **6.5** (0.7) | **16.2** (1.6) | **6.3** (0.5) | **215.0** (11.3) |
| pH 5.75 | **42.7** (1.6) | **2.9** (0.2) | **4.5** (0.9) | **14.1** (0.9) | **4.3** (0.6) | **165.5** (18.2) |
| pH 6.25 | **39.8** (1.2) | **2.8** (0.2) | **2.0** (0.2) | **11.4** (0.6) | **2.3** (0.2) | **99.4** ( 3.8) |
| pH 7.00 | **43.2** (1.9) | **2.5** (0.2) | **0.9** (0.1) | **10.4** (0.4) | **2.0** (0.1) | **74.4** ( 3.5) |
| pH 8.00 | **41.0** (1.8) | **2.4** (0.2) | **1.0** (0.1) | **10.5** (0.7) | **1.6** (0.2) | **77.1** ( 4.6) |
| Cadmium 100 mg/kg | | | | | | |
| pH 3.75 | **18.6** (2.7) | **0.6** (0.1) | **487** (19.6) | **20.0** (1.4) | **7.2** (0.5) | **394.0** (11.6) |
| pH 4.75 | **30.3** (2.8) | **1.5** (0.3) | **329** ( 9.2) | **21.2** (2.6) | **7.1** (1.0) | **289.6** (14.0) |
| pH 5.25 | **29.2** (1.6) | **1.4** (0.1) | **247** (19.3) | **16.2** (0.8) | **5.3** (0.8) | **208.1** ( 8.8) |
| pH 5.75 | **32.5** (1.5) | **1.9** (0.2) | **172** (11.8) | **11.1** (0.3) | **3.6** (0.3) | **145.7** ( 5.5) |
| pH 6.25 | **39.2** (1.4) | **2.2** (0.2) | **68** ( 7.1) | **9.2** (0.5) | **2.6** (0.2) | **93.0** ( 6.0) |
| pH 7.00 | **34.5** (1.8) | **1.8** (0.2) | **41** ( 4.3) | **8.9** (0.5) | **2.2** (0.2) | **69.6** ( 4.4) |
| pH 8.00 | **32.2** (1.7) | **1.3** (0.1) | **30** ( 4.8) | **8.8** (0.4) | **1.9** (0.4) | **53.6** ( 3.4) |
| Zinc 250 mg/kg | | | | | | |
| pH 3.75 | **27.8** (3.1) | **0.8** (0.1) | **19.7** (1.6) | **28.3** (2.2) | **7.9** (1.3) | **1934** (118) |
| pH 4.75 | **39.6** (1.7) | **1.6** (0.2) | **9.9** (0.7) | **20.9** (1.1) | **5.7** (0.5) | **1403** ( 73) |
| pH 5.25 | **41.3** (1.9) | **1.9** (0.1) | **6.4** (0.5) | **14.4** (1.0) | **5.1** (0.6) | **995** ( 50) |
| pH 5.75 | **43.7** (1.9) | **2.3** (0.2) | **5.0** (0.8) | **13.5** (0.8) | **4.1** (0.3) | **915** ( 34) |
| pH 6.25 | **44.0** (1.9) | **3.1** (0.1) | **1.9** (0.3) | **11.0** (1.0) | **2.4** (0.4) | **467** ( 33) |
| pH 7.00 | **43.9** (1.1) | **2.7** (0.2) | **0.7** (0.1) | **10.5** (0.4) | **1.8** (0.4) | **218** ( 10) |
| pH 8.00 | **39.2** (1.1) | **1.9** (0.1) | **0.5** (0.06) | **7.5** (0.4) | **1.5** (0.1) | **129** ( 41) |
| Lead 750 mg/kg | | | | | | |
| pH 3.75 | **30.0** (2.9) | **1.1** (0.2) | **21.4** (2.2) | **25.5** (1.7) | **94.1** (6.8) | **519.5** (24.5) |
| pH 4.75 | **40.8** (1.7) | **1.6** (0.1) | **12.6** (1.3) | **22.8** (1.8) | **70.9** (4.4) | **399.1** (22.3) |
| pH5.25 | **38.6** (1.5) | **1.8** (0.1) | **6.4** (0.5) | **16.3** (0.8) | **54.9** (3.4) | **217.3** ( 8.1) |
| pH5.75 | **44.0** (1.3) | **2.6** (0.2) | **2.9** (0.4) | **11.5** (0.6) | **29.1** (3.4) | **137.6** (11.3) |
| pH6.25 | **40.9** (1.4) | **2.7** (0.2) | **1.8** (0.5) | **10.6** (0.4) | **14.2** (2.4) | **97.1** ( 9.5) |
| pH7.00 | **41.6** (1.6) | **2.4** (0.2) | **0.6** (0.09) | **10.2** (0.5) | **8.1** (0.6) | **70.1** ( 5.9) |
| pH8.00 | **42.9** (1.7) | **2.2** (0.1) | **0.5** (0.07) | **9.3** (0.4) | **7.7** (0.2) | **85.4** ( 4.2) |

**Appendix 9 (cont.)**

| Metal/pH treatments | Shoot weight (grams) | Root weight (grams) | Root/ shoot ratio | Tolerance indices | | |
|---|---|---|---|---|---|---|
| | | | | Shoots | Roots | Total |
| Control | | | | | | |
| pH 3.75 | **1.19** (0.13) | **0.48** (0.05) | **0.40** (0.01) | 1 | 1 | 1 |
| pH 4.75 | **1.86** (0.10) | **0.69** (0.04) | **0.37** (0.01) | 1 | 1 | 1 |
| pH 5.25 | **1.74** (0.10) | **0.61** (0.07) | **0.34** (0.02) | 1 | 1 | 1 |
| pH 5.75 | **2.21** (0.17) | **0.66** (0.04) | **0.31** (0.02) | 1 | 1 | 1 |
| pH 6.25 | **2.12** (0.12) | **0.70** (0.05) | **0.33** (0.02) | 1 | 1 | 1 |
| pH 7.00 | **1.86** (0.14) | **0.67** (0.06) | **0.36** (0.02) | 1 | 1 | 1 |
| pH 8.00 | **1.79** (0.14) | **0.63** (0.07) | **0.35** (0.03) | 1 | 1 | 1 |
| Cadmium 100 mg/kg | | | | | | |
| pH 3.75 | **0.51** (0.11) | **0.11** (0.02) | **0.21** (0.01) | **0.43** | **0.22** | **0.37** |
| pH 4.75 | **1.18** (0.21) | **0.31** (0.08) | **0.22** (0.03) | **0.64** | **0.45** | **0.59** |
| pH 5.25 | **1.09** (0.12) | **0.28** (0.03) | **0.27** (0.01) | **0.63** | **0.46** | **0.58** |
| pH 5.75 | **1.42** (0.13) | **0.48** (0.07) | **0.33** (0.02) | **0.64** | **0.72** | **0.66** |
| pH 6.25 | **1.70** (0.12) | **0.52** (0.05) | **0.31** (0.01) | **0.80** | **0.75** | **0.79** |
| pH 7.00 | **1.41** (0.13) | **0.39** (0.03) | **0.28** (0.01) | **0.76** | **0.58** | **0.71** |
| pH 8.00 | **1.01** (0.09) | **0.29** (0.03) | **0.29** (0.02) | **0.57** | **0.45** | **0.54** |
| Zinc 250 mg/kg | | | | | | |
| pH 3.75 | **0.63** (0.11) | **0.13** (0.02) | **0.27** (0.06) | **0.53** | **0.28** | **0.46** |
| pH 4.75 | **1.34** (0.13) | **0.26** (0.03) | **0.21** (0.02) | **0.72** | **0.38** | **0.63** |
| pH 5.25 | **1.51** (0.11) | **0.36** (0.03) | **0.24** (0.02) | **0.87** | **0.59** | **0.80** |
| pH 5.75 | **1.80** (0.14) | **0.51** (0.08) | **0.28** (0.02) | **0.82** | **0.77** | **0.81** |
| pH 6.25 | **2.37** (0.09) | **0.73** (0.06) | **0.31** (0.02) | **1.12** | **1.04** | **1.10** |
| pH 7.00 | **2.12** (0.12) | **0.58** (0.05) | **0.27** (0.02) | **1.14** | **0.87** | **1.07** |
| pH 8.00 | **1.44** (0.07) | **0.42** (0.04) | **0.29** (0.02) | **0.81** | **0.66** | **0.77** |
| Lead 750 mg/kg | | | | | | |
| pH 3.75 | **0.87** (0.15) | **0.20** (0.03) | **0.25** (0.02) | **0.73** | **0.42** | **0.64** |
| pH 4.75 | **1.36** (0.09) | **0.27** (0.02) | **0.20** (0.01) | **0.73** | **0.39** | **0.64** |
| pH 5.25 | **1.45** (0.10) | **0.32** (0.03) | **0.22** (0.01) | **0.84** | **0.52** | **0.75** |
| pH 5.75 | **2.11** (0.16) | **0.47** (0.04) | **0.22** (0.01) | **0.96** | **0.71** | **0.90** |
| pH 6.25 | **2.15** (0.14) | **0.54** (0.04) | **0.25** (0.01) | **1.01** | **0.77** | **0.95** |
| pH 7.00 | **1.91** (0.14) | **0.49** (0.04) | **0.26** (0.01) | **1.03** | **0.74** | **0.95** |
| pH 8.00 | **1.72** (0.09) | **0.45** (0.02) | **0.26** (0.01) | **0.96** | **0.71** | **0.89** |